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Polishing Industrial Waste Stream Effluents Using Fly Ash - Natural Clay Sorbent Combination

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POLISHING INDUSTRIAL WASTE STREAM EFFLUENTS USING FLY ASH - NATURAL CLAY SORBENT COMBINATION

by

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16. ABSTRACT

A laboratory evaluation of the use of acidic and basic fly ashes, bentonite, bauxite, illite, kaolinite, zeolite, vermiculite, and activated alumina is presented for polishing a 3.8×10^6 liters per day waste stream from the feldspar mining and processing industry. Activated alumina which is used for the removal of fluoride in potable water supplies is included for comparison purposes.

The most effective sorbent for polishing this waste stream, which contained significant concentration of fluoride, iron, lead, chromium and cadmium, was an illite/basic fly ash/lime combination. Design of the treatment process for removal of fluoride also provided effective removals of the cations. Maximum removals of fluoride were achieved at pH of 6.3, and a minimum contact time of 6 hours between the sorbent and waste stream was required for maximum removal of fluoride.

Estimated material costs for the illite/basic fly ash/lime sorbent combination with spent sorbent regeneration are 13.3 cents per 3.8×10^3 liters (1000 gallons) of wastewater. The use of activated alumina with regenerations requires twice this amount. Estimated material costs for sorbents used only once are 45 cents per 3.8×10^3 liters. Disposal of the spent sorbents should pose no problems. Repeated washing showed no significant loss of sorbed cations and anions.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. These studies were undertaken to evaluate in the laboratory the use of natural clay/fly ash sorbent combinations for the polishing of industrial waste stream effluents. These studies were conducted on the effluents collected from the feldspar mining and processing industry. The use of these sorbents can provide an inexpensive system for the treatment of heavy metals and toxic anions present in industrial waste stream effluents.

Such information will be of value both to EPA's regulatory program (Effluent Guidelines Division) and to the industry itself in arriving at meaningful and achievable discharge levels. Within EPA's R & D program the information will be used as part of the continuing program to develop and evaluate improved and less costly technology to minimize industrial waste discharges. Besides its direct application to effluents from metal finishing industry, this technology may find application to treat metal-containing wastes generated by a host of other industries.

For further information concerning this subject the Industrial Pollution Control Division should be contacted.

David G. Stephan
Director
Industrial Environmental Research Laboratory

ABSTRACT

A laboratory evaluation of the use of acidic and basic fly ashes, bentonite, bauxite, illite, kaolinite, zeolite, vermiculite, and activated alumina is presented for polishing a 3.8×10^6 liters per day waste stream from the feldspar mining and processing industry. Activated alumina which is used for the removal of fluoride in potable water supplies is included for comparison purposes.

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SECTION 1

INTRODUCTION

The discharge of industrial waste streams that contain heavy metals, toxic anions, and organics into receiving waters can severely limit its reuse.

The availability of inexpensive waste treatment and effluent polishing processes could be an economic incentive for industry. Thus, this investigation was undertaken to develop an inexpensive industrial effluent polishing process to reduce the concentration of organics, heavy metals and toxic anions that may be found in industrial waste stream effluents to acceptable levels for discharge into receiving water.

The wastewater selected for this investigation is that resulting from mining and processing of feldspar ore, which generates significant volumes of wastewater in the order of 3.8×10^6 liters per day (1 million gallons per day) that range in pH from 4.9 to 6.7. It uses organic flotation agents, sulfuric acid, and hydrofluoric acid to remove the mica and feldspar from the ore. This study was undertaken to investigate the treatment of the heavy metals, toxic anions or organics that may be present in significant concentrations in this waste stream. Also, the levels of fluoride in this waste stream averaged about 6 mg/ℓ which is significantly above the maximum concentration of 1.5 mg/ℓ of fluoride considered acceptable for discharge into ground or surface waters and below the theoretical fluoride residue of approximately 8 mg/ℓ that is achieved by calcium precipitation of the fluoride.

Historically, fluoride wastewaters have been considered difficult to treat especially when one is dealing with fluoride concentrations below 8.0 mg/ℓ. Bentonite, diatomaceous earth, silica gel, bauxite, sodium silicate, sodium aluminate, ferric salts, activated carbon, lime-alum, calcium phosphate, ion-exchangers, magnesium, and activated alumina have been used in a number of studies (1-3) to reduce the fluoride in potable water supplies from approximately 6 mg/ℓ to 1 mg/ℓ. Activated alumina with regeneration was found to be the least expensive for treating the fluoride in drinking water. However, when activated alumina with regeneration was investigated as a means of reducing the fluoride concentration in the feldspar waste stream to acceptable levels, it was found to be technically feasible but too expensive to handle the heavy metal, fluoride bearing waste stream flows encountered in the feldspar industry.

For the past two and one-half years, we have been examining the use of waste products such as acidic and basic fly ashes in combination with clays

such as illite, kaolinite, vermiculite, and natural zeolite, commonly found in soils to treat leachate that is generated from industrial sludges deposited in landfills. The sludges that were used in that investigation were a calcium fluoride sludge (of the type generated by the electronics and aircraft industries), a metal finishing sludge, and petroleum sludge from the American Petroleum Institute gravity separators.

The effectiveness of the above sorbents for removing the hazardous and toxic constituents in these leachates was established and the results have been reported (4). The results indicated that none of the above sorbents alone were effective in removing all the above cations, anions, and organic constituents in the industrial sludge leachates studied. However, the combination of two or more of the fly ashes and clays can be collectively combined with desired permeability characteristics to achieve desired reductions in the concentrations of calcium, magnesium ,copper, nickel, zinc, fluoride, cyanide and organics that are present at measurable levels in the three types of sludge leachate studies. For example, fluoride concentrations in the 7 mg/ℓ to 15 mg/ℓ concentrations range encountered in calcium fluoride sludge leachates was reduced to less than 1 mg/ℓ using these inexpensive fly ash/clay sorbent combinations. Also, leaching from the spent sorbent combinations does not pose any danger to ground or surface water supplies. These studies reveal minimal release of the sorbent contaminants in the presence of extensive washing to simulate the flow of rainwater through the spent sorbents. Thus, these combinations because of their costs can be discarded on land after use. The need for sorbent regeneration and the disposal of the sludge produced from the regeneration is not required as is the case if the more expensive activated alumina is used.

A number of investigators have shown that organics (5-8) (e.g. phenols, surfactants, pyridine, other organics characterized by COD) pesticides (9-11) (e.g. parathion, DDT, dieldrin and heptachlor, herbicidesley, paraguat), heavy metals (12-15) (e.g. lead, cadmium, mercury, zinc, mangenese, copper), and toxic anions (16,17)(e.g.chromium VI, arsenic and selenium) in leachates and waste streams are attenuated by clay minerals, soils and waste products. However, virtually none have explored the use of fly ash/clay sorbent combinations for polishing industrial waste streams for the removal of heavy metals, toxic anions and organics, and identified the parameters which control the removals of heavy metals, toxic anions and organics present in these waste streams.

The objective of this investigation is to establish both the technical and economic feasibility of using inexpensive combinations of fly ash and clays such as illite, vermiculite, kaolinite, bentonite and bauxite and natural zeolites for polishing the wastewater resulting from the feldspar mining and processing industry.

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SECTION 2

CONCLUSIONS

1. On the basis of laboratory tests, the illite/basic fly ash/lime sorbent combination appears to be effective for treating waste streams generated by the feldspar mining and processing industry. The sorbent combination can be added directly to the waste stream and the spent sorbent removed by sedimentation at a loading rate of 1.77×10^4 l/m^2/day (432 gal/ft^2/day). Also, the waste stream can be treated in a sorbent bed operated in an upflow expanded-bed made. A six-foot-deep sorbent bed can treat the above flows at a loading rate of 7400 l/m^2 (180 gal/ft^2). This sorbent combination reduced the iron, lead, chromium, cadmium, and fluoride concentration to levels that are generally acceptable for potable water supplies.

2. Reliance upon gravitational flow through the sorbent bed is impractical for treatment of a feldspar waste stream. The permeability of sorbents limit the treatment to loadings as low as 575 l m^2/day (14 gal/ft^2/day). A sorbent bed with surface area of 6.7×10^3 m^2 (7.2×10^4 ft^2) would be required to avoid ponding at a 3.8×10^6 l/day (1MGD) flow rate.

3. Increasing the gravitational flow through a sorbent bed by increasing the particle size in the bed is not practical for treating large volumes of wastewater. An increase in the particle size results in a decrease in the volume of wastewater that can be treated with a given weight of sorbents. Apparently, the advantage of the increased pore volume of the bed by increasing the particle size is offset by a reduction in the sorbent capacity due to the decrease in particle surface area encountered with the larger particles.

4. The conditions required for maximum removal of the fluoride also provide effective treatment of iron, lead, chromium, and cadmium present in the feldspar waste stream. The maximum sorbent capacity for the removal of fluoride occurs at a pH of 6.3, with a contact time of six hours between the sorbents and wastewater.

5. The material cost associated with the use of illite/basic fly ash/lime sorbent for treating 3.8×10^3 (1000 gallons) of feldspar waste stream with regeneration is estimated on the basis of laboratory scale testing to be one third that associated with the use of activated alumina. These costs amount to 13 cents per 3.8×10^3 and 45 cents per 3.8×10^3 l for the sorbent combination and activated alumina, respectively. The difference is primarily associated with the use of NaOH in the regeneration of activated alumina.

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This eliminates the problem associated with the disposal of a metal hydroxide as CaF_2 sludge from the regeneration process. However, replenishing the spent sorbents with unused sorbents raises the treatment costs to 45 cents per 3.8×10^3 liters. Disposal of spent activated alumina without regeneration would amount to $4.95 per 3.8×10^3 liters.

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SECTION 3

RECOMMENDATIONS

The results of this investigation have shown on a laboratory scale that the use of clay/fly ash sorbent combination for polishing the fluoride, iron, lead, chromium, and cadmium in waste stream flows from the feldspar mining and processing operation appears to be both technically and economically feasible.

A project should be undertaken with the cooperation of Federal agencies and industry to demonstrate the use of the fly ash/clay sorbent combination for polishing the heavy metal, fluoride bearing waste streams on an industrial scale.

The development of inexpensive treatment technology would be useful to industries that have treatment facilities but require additional polishing of their effluents for removal of heavy metals and fluoride to meet State and Federal guidelines.

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SECTION 4

MATERIALS AND METHODS

SORBENTS DESCRIPTION

The sorbent materials that were selected for this study are fly ash, zeolite, vermiculite, illite, kaolinite, activated alumina, bauxite and bentonite. The selection of these materials was based on the consideration of economics, availability, and removal potential.

Fly Ash

Fly ash is a waste product that is separated from the flue gas by electrostatic precipitators at power generation plants. This material is generally dark gray in color and is composed of constituents present in coal or their combustion products. Physically, it is a fine, gritty substance with the individual particles ranging from 0.5 to 100 microns. The principal chemical constituents of fly ash are silica, alumina, iron oxides, sulfur trioxides, and alkali and alkaline earth metals. Approximately 30 million tons of fly ash are produced annually in this country; only 17.4% is eventually utilized, and the balance is disposed of in landfills. The samples, both acidic and basic fly ashes, used for this study were supplied by Public Service Electric and Gas Company, Hudson Generating Station, Jersey City, New Jersey.

Zeolite

Any mineral belonging to the zeolite family of minerals and synthetic compounds is characterized by an aluminosilicate tetrahedral framework and loosely held water molecules permitting reversible dehydration. Zeolites have been extensively studied from theoretical and technical standpoints because of their potential and actual use as molecular sieves, catalysts, and water softeners. Zeolites are low temperature and low-pressure minerals found in aurygladoidal basalts and also as authigenic minerals in sandstones and other sediments. These materials are usually white in color. The natural zeolite used in this study was obtained from Brickhor, New Mexico, and was furnished by the Double Eagle Petroleum and Mining Company, Casper, Wyoming. Physically, the material is light tannish-white in color and has a powder-like texture. The zeolite sorbent was used as received.

Kaolinite

The structure of kaolinite is composed of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit. It is the principal mineral of the kaolinite group of clay mineral. The mineral

kaolinite has a moderately low cation-exchange capacity (5-15 milliequivalent per 100 g). Broken bonds around the edges of the silica-alumina units are the major cause of this exchange capacity. Kaolinite may form under acid conditions at low temperatures and pressures. It is a principal component of lateritic-type soils. Kaolinite has been used extensively in the ceramics industry and in paper products. The selection of this sorbent material was principally due to its importance in clay family as well as its potential sorptive properties and availability. This material was furnished by Georgia Kaolin Company, Elizabeth, New Jersey. Physically, it is tannish-white powder. It was used as received.

Vermiculite

This micaceous mineral exfoliates when heated or subjected to certain chemical reactions. It is a hydrated magnesium aluminum iron silicate. The structure of vermiculite consists of trioctahedral mica sheets separated by double water layers and is unbalanced by substitution of aluminum for tetrahedral layer. The resulting charge deficiency is satisfied by exchangeable cations which occur chiefly between the mica layers. Vermiculites have a high cation-exchange capacity (150 milliequivalents per 100 g). They also absorb certain organic molecules between the mica layers. It is frequently listed as an alternate product of biotite mica in ancient sediments. Vermiculite is extensively used in many industries, including fireproofing, insulation, fertilizer conditioners, and packing materials. This material was used as received and was obtained from W. R. Grace & Co., Trenton, New Jersey.

Illite

The term illite is used to denote the aluminum, magnesium, and iron rich mica found in the clay fraction of weathered shale in Illinois. The basic structural unit is composed of two silica tetrahedral sheets with a central octahedral sheet. The size of naturally occurring illite particles is very small with well-defined edges. The illites have a moderate cation-exchange capacity (20-30 milliequivalent per 100 g). It is primarily due to broken bonds, but lattice substitution may also be a cause in poorly crystallized varieties. Illite is a common product of weathering and is particularly abundant in deep-sea clays. The material used for this study was obtained from A. P. Green Refractory Co., Morris, Illinois.

The material received was in rock form and was ground to powder that passed through an 80-mesh screen before use.

Activated Alumina

Activated alumina is a highly porous, granular form of aluminum oxide with preferential adsorptive capacity for moisture and odor. Sizes range from powder to 1.5-inch diameter particles. In this study, particle sizes ranging from 0.147 mm to 0.295 mm were used. Activated alumina has been used as a desiccant for gases and vapors in the petroleum industry. It is also used as a catalyst or catalyst carrier. The material studied was furnished by Alcoa, located in Bauxite, Arkansas.

Bauxite

Bauxite is an aluminum ore and consists of the mineral gibbsite ($Al_2O_3 \cdot 2H_2O$) and/or boehmite ($Al_2O_3 \cdot 2H_2O$). It is a common residual or transported constituent of clay deposits in tropical and sub-tropical regions. Bauxite is the principal commercial source of aluminum, and has been studied extensively by economic geologists. The selection of this material was principally due to its aluminum content. The material was obtained from A. P. Green Refractory Co., Mexico, Missouri.

Bentonite

Bentonite has a three-layer sheet structure which is composed of two layers of silica tetrahedrons and one central dioctahedral alumina layer. This material is highly colloidal, plastic swelling, and impermeable. It has a very large range of cation exchange capacity. Bentonite possesses important and unique properties which give them great commercial value. The selection of this material was principally due to its important characteristics as a clay material. The material was used as received and was obtained from Whittaker, Clark and Daniels, Inc., South Plainfield, New Jersey.

PREPARATION OF SORBENT MATERIALS

All sorbent materials were used as received. Sorbent materials which were not obtained as a powder (illite and vermiculite) were ground in a laboratory hammer mill (Weber Bros., and White Metal Works, Inc. Type 22) and passed through an eighty mesh A.S.T.M. standard sieve. All sorbents were dried to constant weight at 103°C in accordance with "Standard Method" procedures and stored in a desiccator until used.

Static Studies

A measured amount of dried sorbent material was placed into a tared one liter screw capped polypropylene Erlenmeyer flask. The flask was sealed and agitated for 24 hours at ambient temperature. The mixture was then filtered through a glass fiber filter and the filtrate was analyzed.

Dynamic Studies

Lysimeter studies were conducted to evaluate hydraulic conditions and removal capacity of the sorbents for the specific contaminants present in significant concentration in the wastewater under dynamic conditions. Two hydraulic systems, gravitation flow and expanded bed flow were investigated.

Gravitational Flow

Lysimeters were constructed of plexiglass tubing (6.2 cm i.d.; 0.6 cm wall thickness; 90 cm length), supported in a vertical position. The laboratory arrangement of the lysimeters are shown in Figure 1. A 164 micron pore size corundum disc (6.10 cm diameter; 0.6 cm thickness) was placed in each column, directly over the drain hole in order to prevent clogging of the

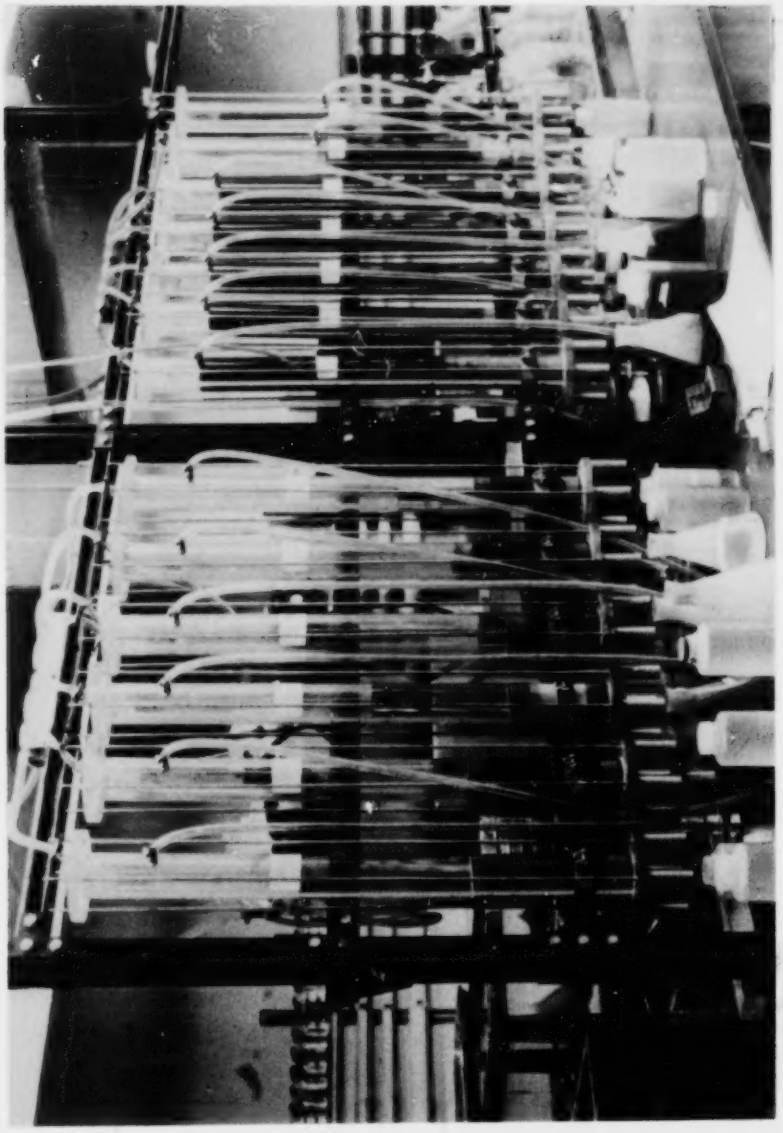

Figure 1. Laboratory arrangement of lysimeters.

outlet and also to support the sorbent material. The column was packed with the preweighed sorbent, placing 3 to 4 cm of Ottawa sand below and above the sorbent to prevent disturbing the geometry of the sorbent column during addition of leachate or water. The packed column was then slowly wetted with waste water to allow total saturation and to force all entrapped air in the soil voids out of the column packing. After a saturation period of at least 24 hours, the column was then filled with wastewater to the level of an overflow drain, which had been trapped into the top side of the column, to permit a constant head condition. Wastewater was fed to the top of the column through a valved manifold that distributed the leachate to 10 lysimeters simultaneously from a central reservoir. The central reservoir, a 100 liter polyethylene vessel, delivered the leachate to the manifold system by means of a gravity syphon feed arrangement. Any overflow from the constant head drains was collected and pumped back up to the central reservoir. All tubing in the system was made of Tygon tubing (.95 cm i.d.). A constant hydraulic head was maintained in the lysimeters at all times, and the volume of waste water through the columns was continuously monitored. Samples of waste water effluent were collected at intervals and analyzed to determine the concentration of all measurable constituents remaining in the effluent after a known volume of wastewater had passed through the column. This was continued until breakthrough for all measurable contaminants had occurred or excessively low permeabilities were encountered. Breakthrough is defined as that condition when the concentration of the species of concern in the collected effluent sample approached or exceeded that in the influent.

Three different sizes of sorbent particles, (diameters greater than 0.042 cm, between 0.042 cm, and 0.0083 cm, and smaller than 0.0083 cm), were selected for these studies. The amount of sorbent used in the lysimeter were 500 grams and 250 grams. The sorbent combination consisted of a 50 percent mixture of illite and basic fly ash and lime. A series of experiments indicated that the addition of 13 mg of lime to one gram of the illite/fly ash mixture would raise the pH of the feldspar waste water to 6.3 for optimum removal of the cations and anions. Wastewater was fed from overhead reservoirs into the lysimeters under constant head conditions until breakthrough for the anions and cations occurred.

Upflow Expanded Bed Operation

An upflow expanded bed approach was investigated to overcome low permeability exhibited by the sorbents combination. Using the same lysimeter and sorbent bed layout as in the gravitational flow study, the wastewater was fed from the reservoir through the bottom of the bed at a velocity sufficient to expand the bed without loss of the sorbent in the overflow. A flow of 6×10^{-3} gal/min was achieved in lysimeter containing 750 grams of the illite/basic fly ash mixture and 10 grams of lime without loss of sorbent. The effluent was collected from the overflow outlet and volume monitored continually. The collected effluent samples were analyzed for all pollutants of interest until breakthrough had occurred.

Regeneration

Regeneration of the sorbents was investigated to further reduce the costs associated with the use of the clay/fly ash sorbent combinations as well as eliminate the need for stock-piling of the sorbents. Since sulfuric acid is used as part of the flotation process by the feldspar industry, and our earlier studies (4,18) reveal that leaching of heavy metals and anions are enhanced under strongly acidic conditions, regeneration using sulfuric acid was examined.

The regeneration studies were carried out under batch conditions on spend sorbent combinations. Different volumes of a one percent solution of sulfuric acid was added to 10 grams of spent sorbents and shaken for six hours. A series of tests showed that six hours is required for maximum regeneration of the spent sorbent for each specific volume of sulfuric acid solution used. After each regeneration step, the 10 grams of sorbent combinations was filtered, washed, and 0.2 gm of lime added. The sorbent combination was then mixed with the 0.5 liters of feldspar wastewater according to the static studies described earlier. This was repeated for different volumes of one percent sulfuric acid solution until maximum recovery of the spent sorbent as indicated by its sorbent capacity was achieved.

ANALYTICAL PROCEDURES

The constituents in the feldspar wastewater were initially identified using emission spectroscopy. Their concentration was then determined using atomic absorption and specific ion probes (Orion Model 701 Digital pH/mv Meter). The concentration of organics was determined using chemical oxygen demand (COD) measurements; pH measurements were also carried out.

pH Measurements

The pH of the samples was measured by means of an Orion Model 701 Digital pH/mv Meter using an Orion combination pH electrode, Model 91-02.

Chemical Oxygen Demand (COD)

An automated procedure based on the manual method described in "Standard Methods" was employed in the determination of COD. The sample was digested with a potassium dichromate - sulfuric acid digestion mixture, and the depletion of the hexavalent chromium (due to the oxidation reaction with the samples) was measured colorimetrically. This automated analyses was performed using a Technicon Autoanalyzer II (Industrial Method Number 137-71W).

Total Organic Carbon (TOC)

Measured by use of the Dohrmann Envirotech DC-52D Carbon Analyzer.

Determination of Anionic Species

The analysis of the anions Cl^-, F^-, CN^- were as follows:

Chloride Ion Analysis -- Analysis of chloride ion was conducted using a chloride ion electrode (Orion Model No. 94-17) in combination with a single junction reference electrode (Orion Model No. 90-01) connected to an Orion Model 701 digital pH/mv meter. The chloride content of a sample solution was determined directly by comparing the electrode potential reading in the sample solution to electrode potentials obtained in standards of known chloride content. Straight-line calibration curves were obtained over the range of 1 ppm to 1000 ppm using reagent grade sodium chloride.

Fluoride Ion Analysis -- Analysis of fluoride ion was carried out using a fluoride ion electrode (Orion Model 94-09) in combination with a single junction reference electrode (Orion Model 90-01) connected to an Orion Model 701 digital pH/mv meter. The fluoride content of a sample solution was determined directly by comparing the electrode potential reading in the sample solution to electrode potentials obtained in standards of known fluoride content. Straight-line calibration curves were obtained over the range of 0.1 ppm to 1000 ppm using reagent grade sodium fluoride. A total ionic strength adjustor buffer containing 1,2-cyclohexylene dinitrilo tetra-acetic acid (Orion Cat. No. 94-09-09A) was used in the ratio of one part reagent to one part sample for all fluoride ion measurement. This reagent will "swamp out" variations in the levels of other ions present in the solution as well as destroy polyvalent cation complexes of fluoride by preferentially complexing these cations. Therefore, total fluoride was measured.

Analysis of Cyanide Ion -- Analysis of cyanide ion was conducted using a cyanide ion electrode (Orion Model 900100) connected to an Orion Model 701 digital pH mv meter. This electrode responds directly to cyanide ion activity, without regard to sample ionic composition, total ionic strength, pH or complexing species. The free cyanide ion content of a sample solution was determined directly by comparing the electrode potentials obtained using standards of known free cyanide ion content. Semi-logarithmic calibration curves were obtained over the range of 0.01 to 10 ppm using reagent grade sodium cyanide. All solutions were adjusted with 10M NaOH to concentrations of 0.1M in NaOH.

Determination of Metals

The concentrations of the various metals reported (i.e., Ca, Cd, Cr, Cu, Fe, Mg, Ni, Pb, Zn) were determined using a Varian Techtron Atomic Absorption Spectrometer (Model 1200) according to E.P.A. procedures (15). The reference solutions used to construct calibration curves in these determinations were made up using deionized water with a specific resistance of 18 Megohm-cm (25°C).

PERMEABILITY STUDIES

After a steady flow condition through the lysimeter was established, volume throughput per second was recorded. The permeability coefficient, k, was then calculated by means of the following equation:

$$k = (QL)/(aht)$$

where a = Cross-sectional area of soil column

Q = Total quantity of water which flowed through the soil column in elapsed time, t

h = Total hydraulic head, i.e., distance from the bottom drain to the top of the leachate level corresponding to the level of the top overflow drain

L = Length of soil sample in the lysimeter

t = Total elapsed time in seconds for quantity collected, Q

SECTION 5

RESULTS AND DISCUSSION

ANALYSIS OF FELDSPAR WASTEWATER

Three separate effluent samples were collected from a feldspar mining and processing operation over a period of one year. The results of the analysis of these samples are listed in Table 1. An examination of the heavy metals and toxic anions reveal that the iron and fluoride were at concentration levels in the three samples that should be reduced. The iron ranged from 0.3 mg/ℓ to 4.5 mg/ℓ and the fluoride from 4.0 mg/ℓ to 17.5 mg/ℓ. Reduction of the cadmium, chromium, and lead concentrations in sample 3 were also addressed.

Evaluation of Sorbents

The sorbents, bentonite, bauxite, acidic and basic fly ash, illite, kaolinite, natural zeolite and vermiculite, were screened for their effectiveness in reducing the fluoride ion in the waste stream to below 1.5 mg/ℓ. Different specific quantities of sorbent were mixed with a given volume of wastewater samples for 24 hours and the amount of fluoride remaining in solution was measured. Both illite and kaolinite showed comparable removals in reducing the fluoride concentrations to below 1.5 mg/ℓ (Figure 2). Bentonite, bauxite, acidic fly ash, zeolite and vermiculite were unable to reduce the fluoride concentration to below 1.5 mg/ℓ even when sorbent concentrations of 100 mg/ℓ were used.

These findings are in agreement with earlier reported results (4) with waste samples obtained from other sources. The illite and kaolinite were found to be most effective for treating the fluoride in acidic, neutral and basic industrial sludge leachates.

Acidic and basic fly ash, kaolinite and illite were examined for their effectiveness in reducing the iron concentration in the wastewater. Different quantities of sorbent were mixed with a given volume of wastewater for 24 hours and the amount of iron remaining in solution was measured. Basic fly ash, which was found to be the most effective sorbent for the removal of iron, required a sorbent concentration of only 1 mg/ℓ to reduce the iron concentration to 0.02 mg/ℓ. This finding agrees with our earlier results (18) where the basic fly ash was also found to be the most effective sorbent for treating the iron in industrial sludge leachates. The next best sorbent is kaolinite which reduces the concentration to 0.1 mg/ℓ, followed by illite and acidic fly ash which reduces it to 0.2 mg/ℓ (Figure 3).

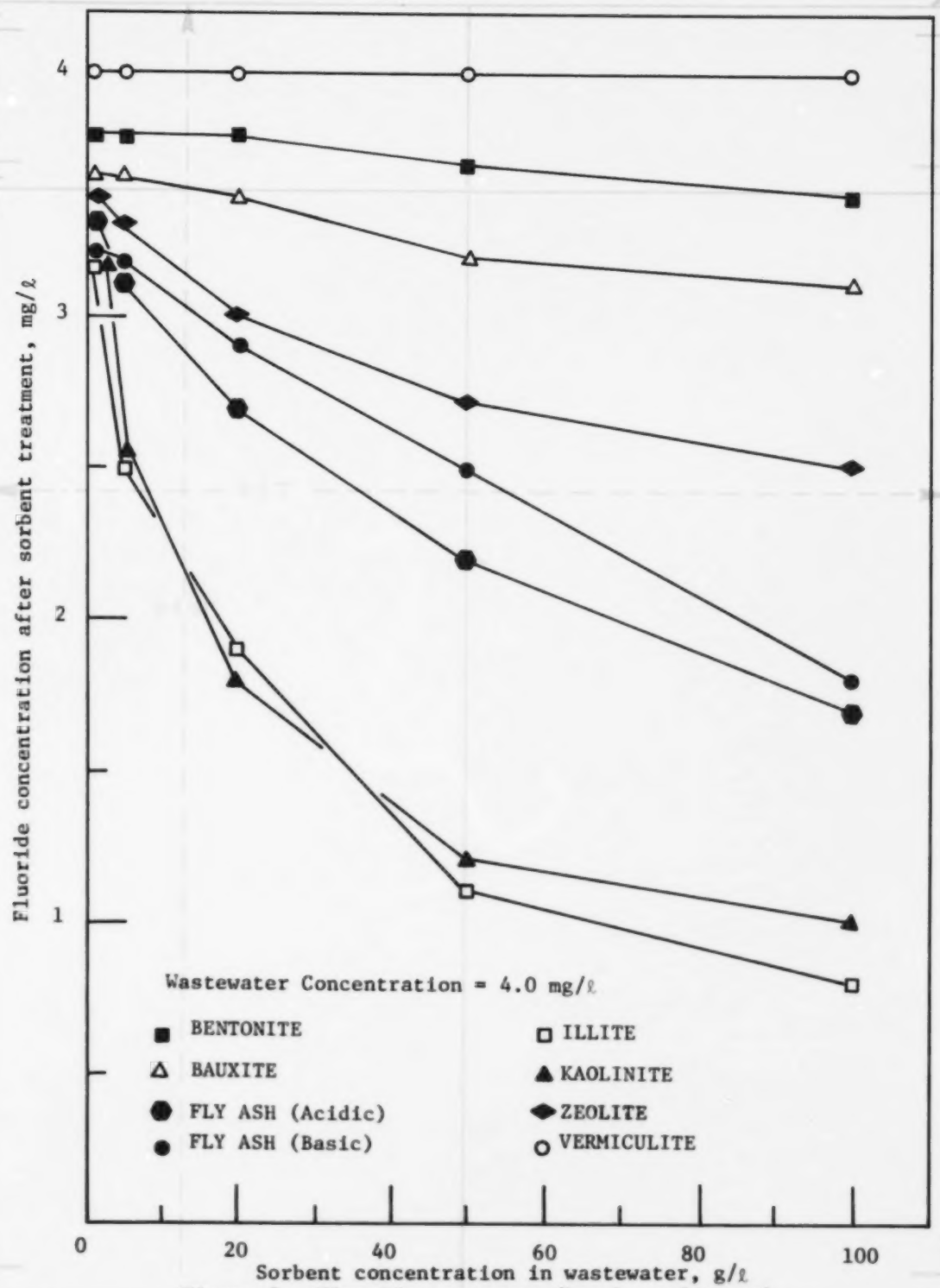

Figure 2. Fluoride treatment (batch conditions)

TABLE 1. ANALYSIS OF FELDSPAR WASTEWATER

Contaminants	Concentration mg/ℓ Sample 1	Sample 2	Sample 3
F	4.0	17.5	5.8
Cl	27	32	39
CN	0.0	0.009	0.008
SO_4	64	82	57
Ca	5.2	6.7	11.3
Cd	0.009	0.007	0.015
Cr	0.007	0.008	0.05
Cu	0.035	0.047	0.02
Fe	1.8	4.5	0.3
Mg	1.7	3.7	1.9
Ni	0.054	0.044	0.15
Pb	0.019	0.013	0.12
Zn	0.054	0.076	0.18
COD	14	20	18
pH	5.5	4.9	6.3

Effect of pH on the Sorbent Capacity

In our earlier studies (4), pH was shown to have an effect upon the sorbent capacity for the removal of fluoride ion. The sorbent capacity represents the amount of contaminant that will be removed in a waste stream by one gram of sorbent. This was also found to be the case in this study. Increasing the pH of the wastewater from 3 to 7 showed the sorbent capacity for illite and kaolinite for fluoride to be dependent upon pH, but in a different manner. The sorbent capacity for the kaolinite exhibited a fairly broad maximum in the pH range from 3.0 to 4.5, but decreased with an increasing pH above 4.5 (Figure 4). On the other hand, the sorbent capacity for the illite increased to a maximum of a pH of 6.3 followed by a decrease in capacity at higher pH. The maximum sorbent capacity exhibited by the illite is 4.2 times greater than that exhibited by the kaolinite.

Control of the pH of the wastewater is important for achieving maximum removals of a contaminant. If one does not adjust the pH of the wastewater to that which provides maximum removals of the contaminant, then the effectiveness of the treatment system is reduced. For example, the treatment of the feldspar wastewater with the same amount of illite and kaolinite, and without pH adjustment of the wastewater, showed similar concentration of fluoride remaining in the wastewater. The pH of wastewater ranged from

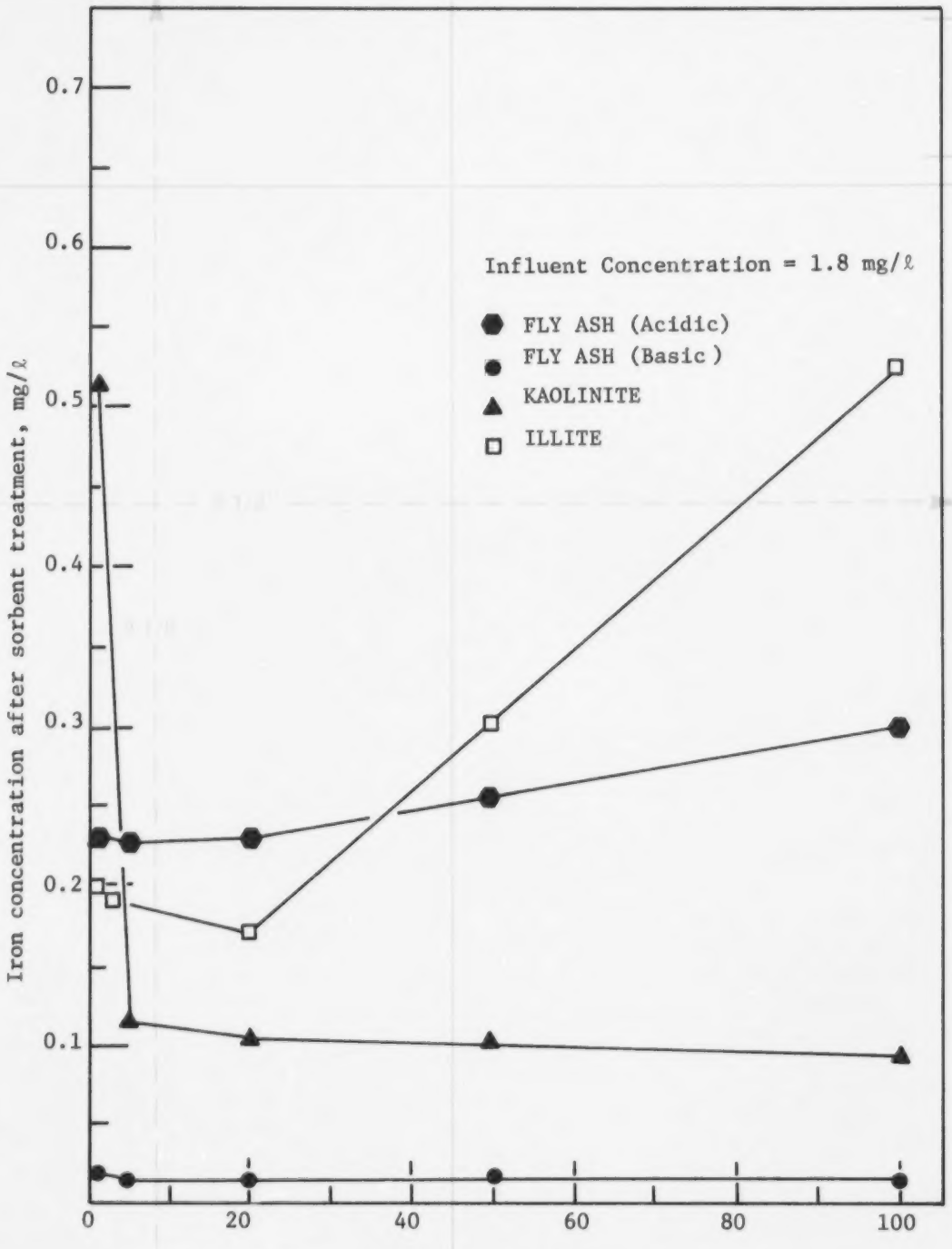

Figure 3. Iron treatment (batch conditions)

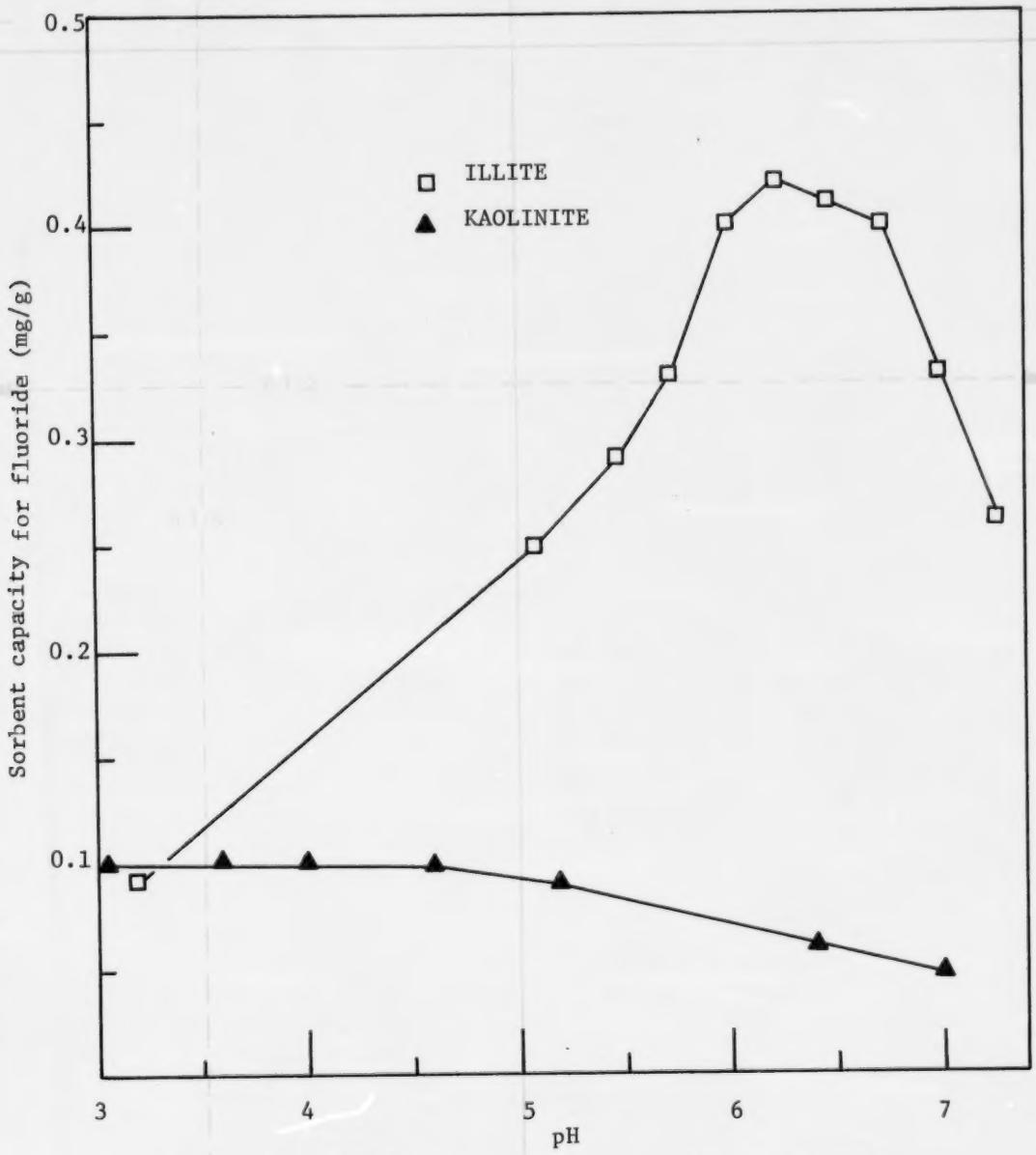

Figure 4. pH effect on sorbent capacity for fluoride (batch conditions)

5.4 to 5.0 and 4.5 to 3.0 for the kaolinite and illite, respectively (Figure 5). If the pH of the wastewater were adjusted to 6.3, the illite would be 4 times more effective than the kaolinite in reducing the fluoride ion wastewater concentration.

The removal of iron by the basic fly ash also shows a dependence on pH. The iron in the wastewater shows a reduction in concentration as the pH is increased from 6.4 to 9.2 (Figure 5). Further reductions in the iron concentration below 0.02 mg/ℓ due to alkaline precipitation under basic condition was not observed since the iron remaining in the wastewater showed a slight decrease but remained essentially constant over this pH range (Figure 3).

These results indicate that maximum removals of iron can be achieved at the same pH required for maximum removal of the fluoride.

Relationship Between Sorbent Capacity and Desired Concentration

The amount of pollutant that will be removed by adding a specific amount of sorbent to a specific volume of feldspar wastewater is defined by the sorbent capacity. As greater amounts of pollutant removal are required in the treatment of a given waste stream to provide lower effluent concentrations, a smaller sorbent capacity is used to define the amount of sorbent required. The reason is that the sorbents become less effective with lower desirable effluent concentrations. For example, if the concentration of fluoride in the waste stream is 8 mg/ℓ and the desired effluent concentration is 5 mg/ℓ, 3 g of sorbent would be required in 1 liter of waste stream to remove the 3 mg of fluoride based upon a sorbent capacity of 1 mg/g (Figure 6). However, if the fluoride concentration in the waste stream is 4 mg/ℓ, and the desired fluoride effluent concentration is 1 mg/ℓ, 3 mg of fluoride will be removed. However, this removal will require 10 g instead of 3 g of sorbent based upon a sorbent capacity of 0.3 mg/g. In other words, the sorbent combination is about three times more effective in removing 3 mg of fluoride from a waste stream containing 8 mg/ℓ of fluoride than from waste stream containing 4 mg/ℓ of fluoride.

Contact Time

A minimum contact time of 6 hours between the sorbents and feldspar waste stream sample is required to insure maximum removals of the fluoride. Contact periods less than 6 hours result in greater concentration of the fluoride remaining in the effluent after treatment (Figure 7).

Our earlier studies (4) indicate similar findings. The extent of removal of fluoride and COD in calcium fluoride sludge leachate depend upon the contact time between the sorbents and the leachate. As the contact time is decreased, the extent of removal of a specific contaminant also decreases.

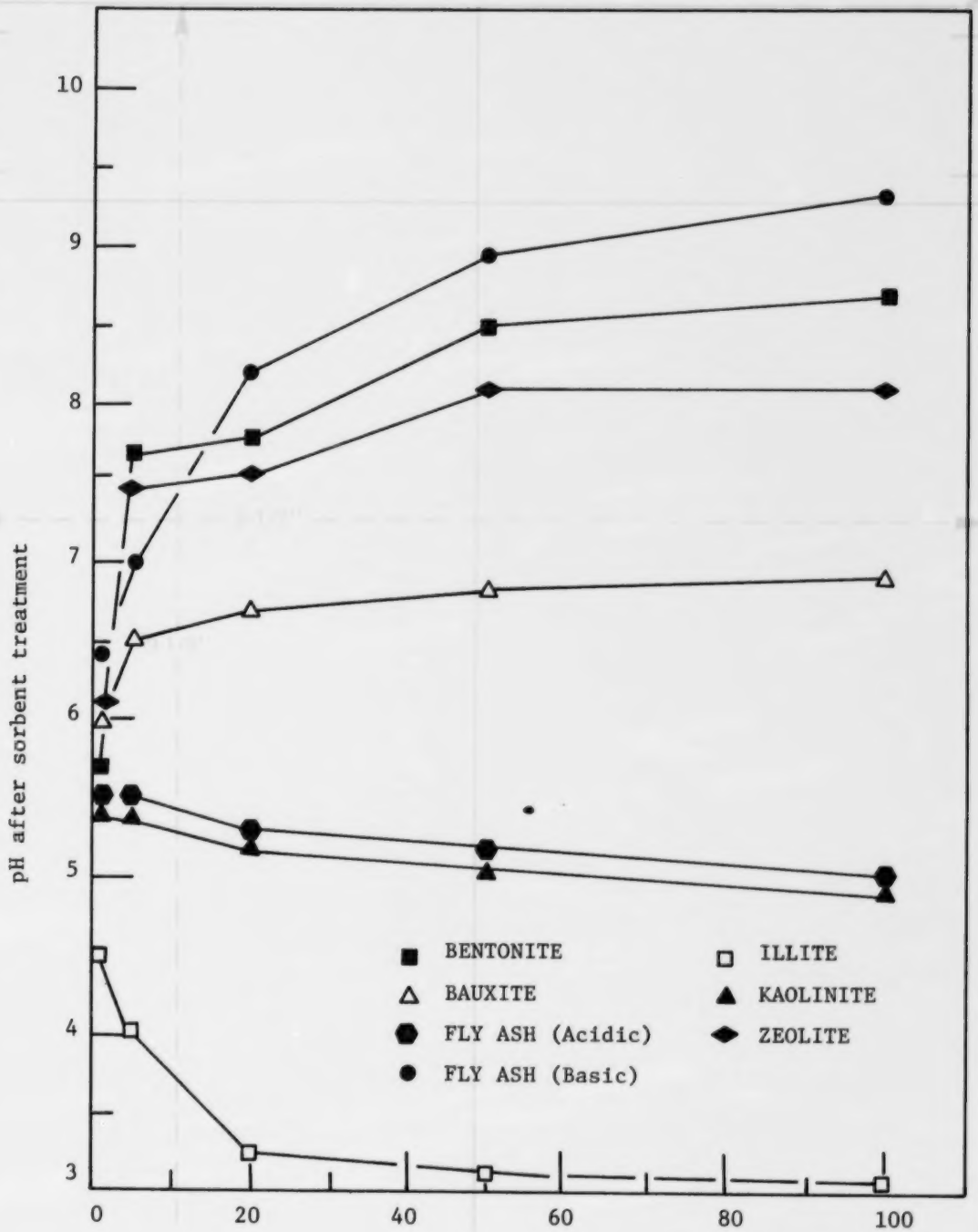

Figure 5. pH dependence on sorbent concentration (batch conditions)

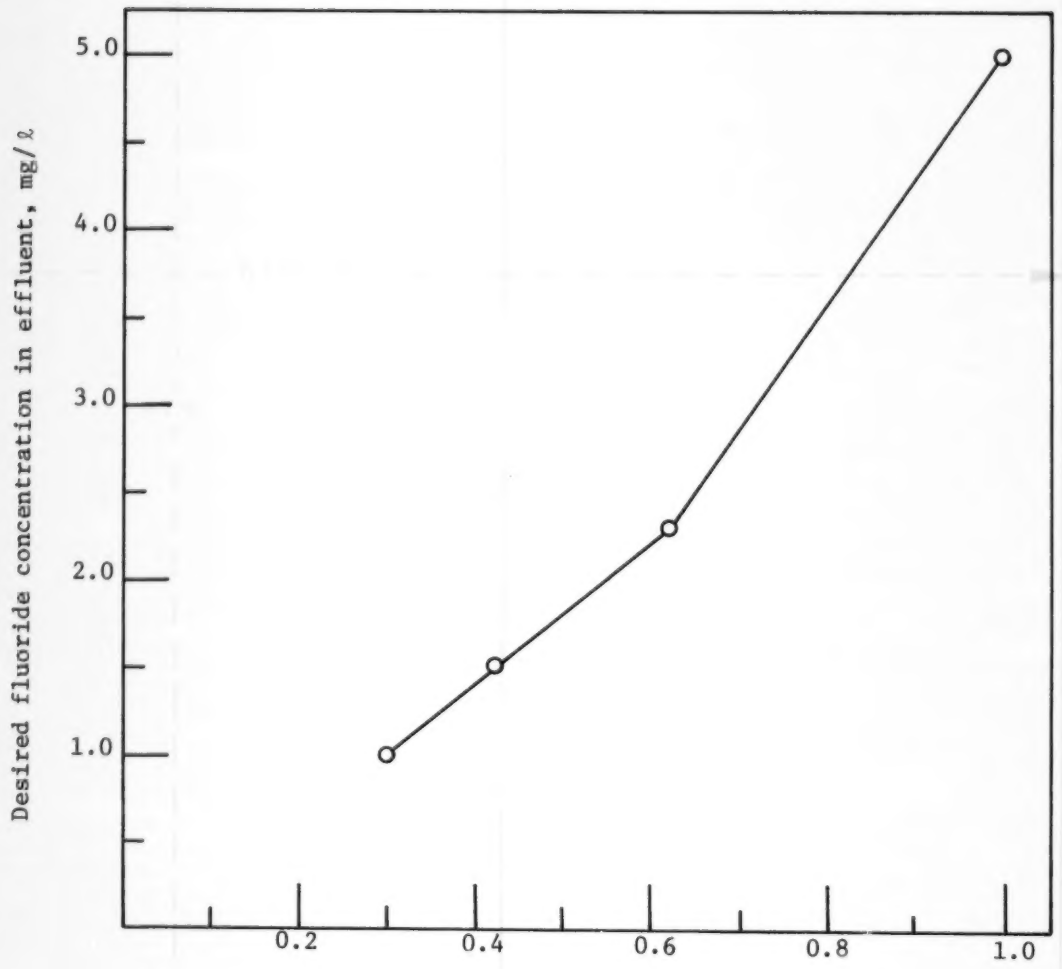

Figure 6. Sorbent capacity versus desired effluent concentration (batch conditions)

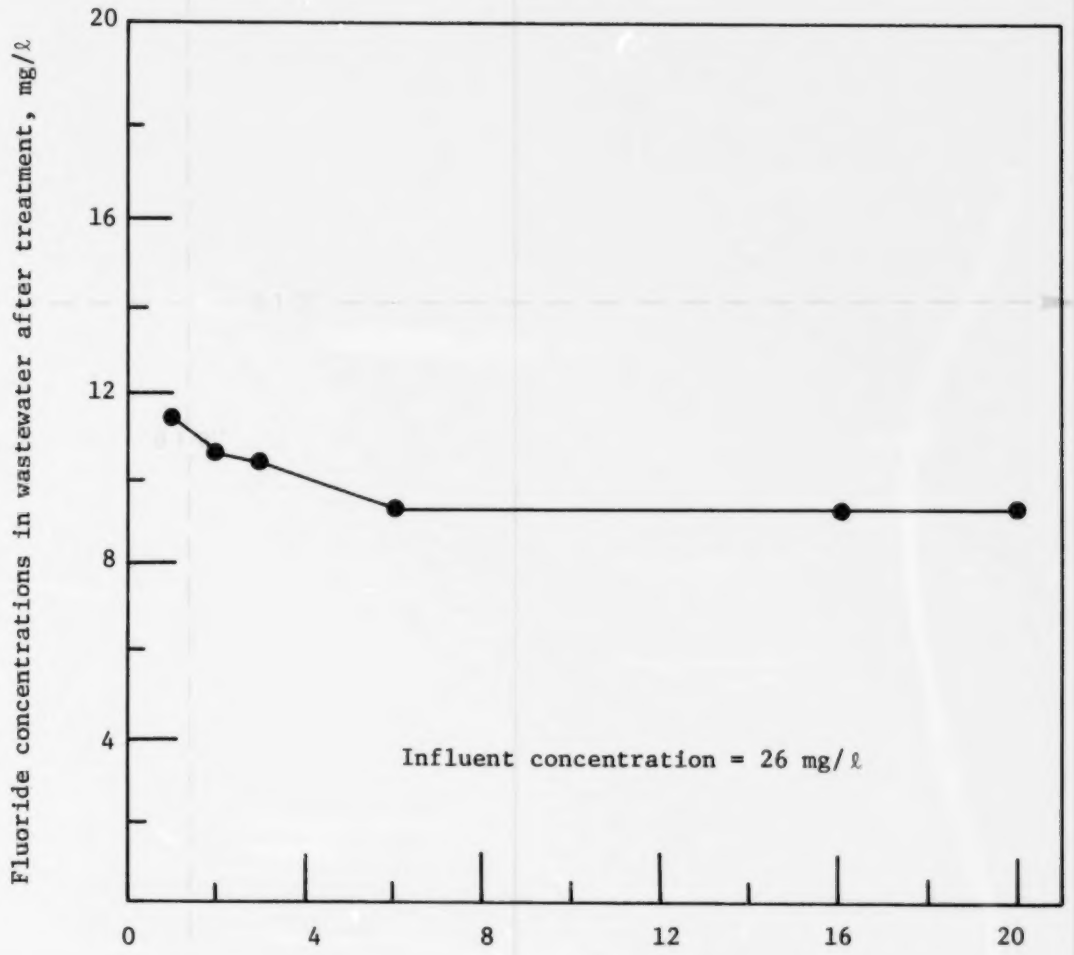

Figure 7. Fluoride influent concentration versus contact time (batch conditions)

RESULTS OF LYSIMETER STUDIES

Lysimeter studies were carried out to determine the effectiveness of the illite-basic fly ash-lime combinations in reducing the fluoride and iron to acceptable levels under flowing conditions. Addition of specific amounts of the most effective sorbents, illite and basic fly ash, to a feldspar waste stream adjusted to a pH of approximately 6.3 with lime, can reduce the fluoride in feldspar wastewater under batch conditions to concentrations of 1.0 mg/ℓ and 0.02 mg/ℓ respectively.

Particle Size and pH Effects on Iron and Fluoride Removed under Flowing Conditions

Different sorbent particle sizes were examined in the lysimeters to determine whether increasing the particle size would allow flows of the order of 3.8×10^6 liters per day (1 mgd) to be handled by sorbent beds under gravitational feed.

The results of using a 50% mixture of illite-basic fly ash whose particles are: 1) in the size range greater than 0.42 mm; 2) between 0.21 and 0.42 mm; and 3) less than 0.21 mm to treat the feldspar waste stream with no pH adjustment, reveal that the two smaller particle size ranges reduce the fluoride to below 1 mg/ℓ in the treatment of 8 liters of waste stream. The particles greater than 0.42 mm only reduce the fluoride to these levels in the treatment of 5 liters of waste stream (Figure 8). The symbols with the same shape are the results of two separate experiments run simultaneously.

In contrast, the sorbent particle size range does not appear to influence the reduction in the iron concentration to 0.12 mg/ℓ with the exception of the initial liter of wastewater passed through the lysimeter (Figure 9). The sorbent whose particle sizes are less than 0.21 mm exhibited the poorest removal followed by the particles in the 0.21 mm to 0.41 mm range, and those greater than 0.41 mm in increasing order, respectively. The initial acidic pH of 3.6 encountered from the lysimeter containing the smallest sorbent particles (Figure 10) is probably responsible for the poorest removal of iron encountered in the initial liter of effluent collected from the lysimeters. Adjustment of the pH of the influent with lime to provide a pH of 4 in the initial effluent from the lysimeter containing the smallest particle size results only in iron removals that are comparable with the larger particles, but also results in improved removals of fluoride.

Breakthrough of fluoride in the lysimeters where the pH of the influent was adjusted to 6.3 occurs after 7 liters of wastewater was passed through these lysimeters. In comparison, breakthrough for the influent where the pH was not adjusted occurs after only 5.5 liters of wastewater was passed through this lysimeter (Figure 11). These results are as expected since it was shown earlier that the maximum removal of the fluoride occurs at a pH of 6.3.

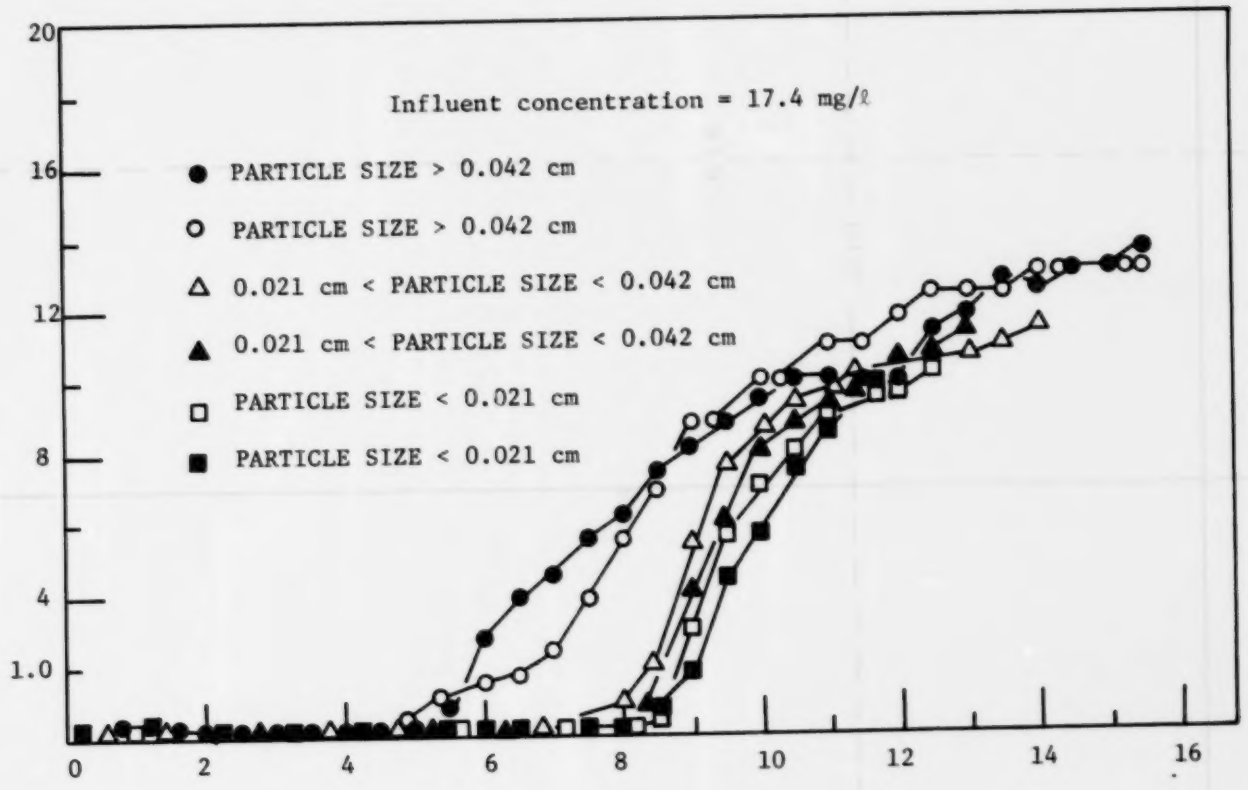

Figure 8. Fluoride removal dependence on sorbent particle size (gravitational flow)

Particle Size Effect on Flow

The permeability exhibited by the sorbents increases with particle size. The sorbents in size range less than 0.21 mm, between 0.21 mm and 0.42 mm, greater than 0.42 mm increased from 1.5×10^{-4} cm/sec, to 3×10^{-4} cm/sec and to 6.5×10^{-4} cm/sec respectively (Figure 12). These permeabilities limit the flows through the lysimeters to only 11.4×10^{-5} ℓ/min (3×10^{-5} gal/min), 15.2×10^{-5} ℓ/min (4×10^{-5} gal/min), and 30.4×10^{-5} ℓ/min (8×10^{-5} gal/min), respectively. These flows provide contact times between the sorbent and waste streams of 61. 1 hours, 44 hours, and 23 hours which are significanly longer than the 6 hours contact time shown earlier to be required for maximum removal of the fluoride ion under batch conditions.

The above results indicate that an actual sorbent bed six feet deep would only be able to handle gravitational flows that range from 132 ℓ/m^2/day (3.2 gal/ft^2/day) to 575 ℓ/m^2/day (14 gal/ft^2/day) to avoid ponding. A sorbent bed six feet deep with a contact time of 6 hours should be able to handle flows of 7420 ℓ/m^2/day (180/gal/ft^2/day).

Flows of 7420 ℓ/m^2/day under the influence of gravity, can be achieved by increasing the size of the particles in the bed. However, an increase in particle size results in a significant decrease in the effectiveness of the sorbent bed for removal of fluoride in specific volumes of wastewater (Figure 8).

Upflow Expanded Bed Treatment

The operation of the lysimeters in an upflow expanded bed mode was investigated since the permeabilities encountered with the sorbents limit gravitational flow.

The maximum possible upflow that could be achieved in the lysimeters which contained a mixture of 750 grams of illite and basic fly ash, and 10 grams of lime without the loss of sorbent was 22.8×10^{-3} ℓ/min (6×10^{-3} gal/min). This is at least two orders of magnitude greater than the above gravitational flows obtained with the same sorbent combination. In an actual six feet deep sorbent bed, a flow of 22.8×10^{-3} ℓ/min in the lysimeter would be equivalent to a treatment rate of about 2.8×10^4 ℓ/min^2/day (680 gal/ft^2/day).

In these experiments, 13 mg of lime was mixed with one g of 50 percent illite-basic fly ash to neutralize the acidic properties of the clay. It was also added to the lysimeter influent to provide a pH of around 6.3 (Figure 13) for maximum removals of the iron and fluoride.

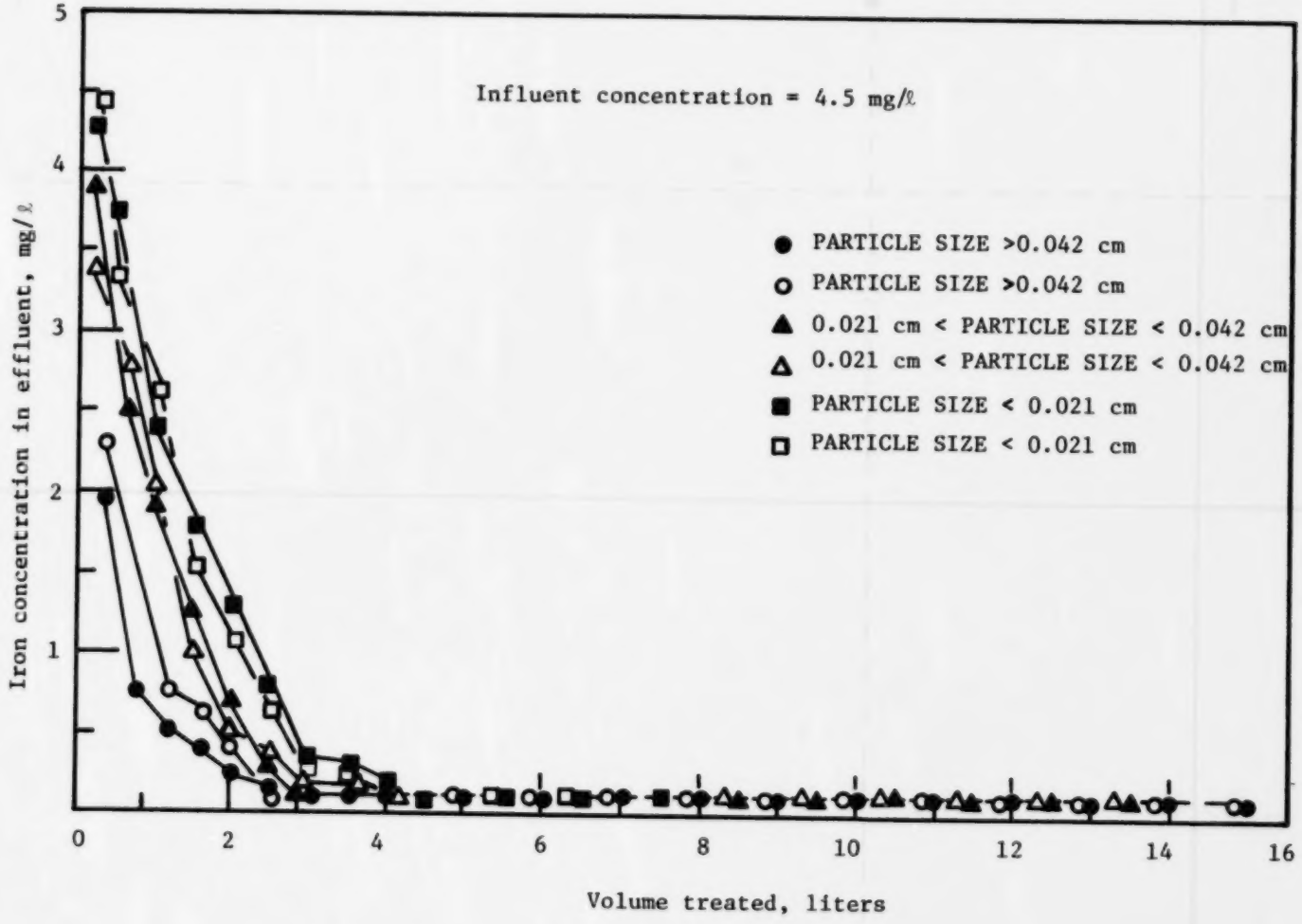

Figure 9. Iron removal dependence on sorbent particle size (gravitational flow).

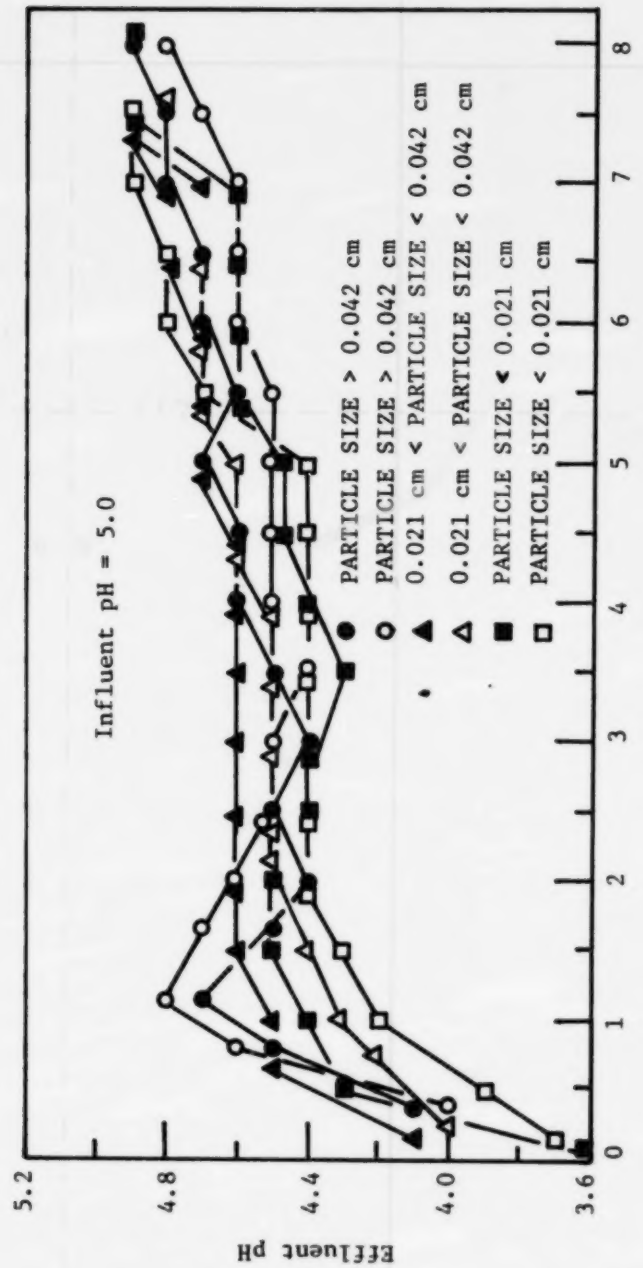

Figure 10. Effluent pH variations (gravitational flow).

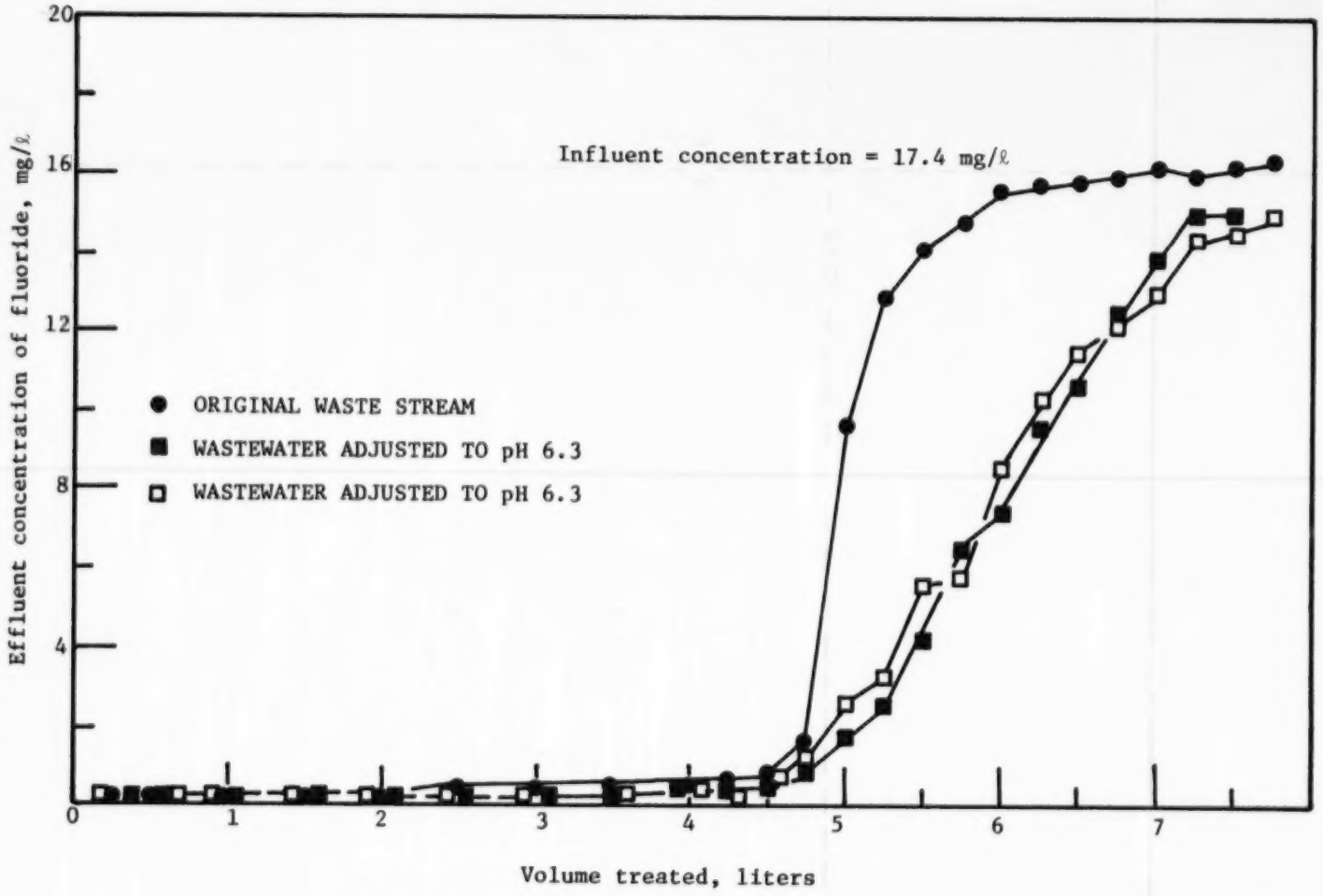

Figure 11. Fluoride treatment with pH adjustment (gravitational flow).

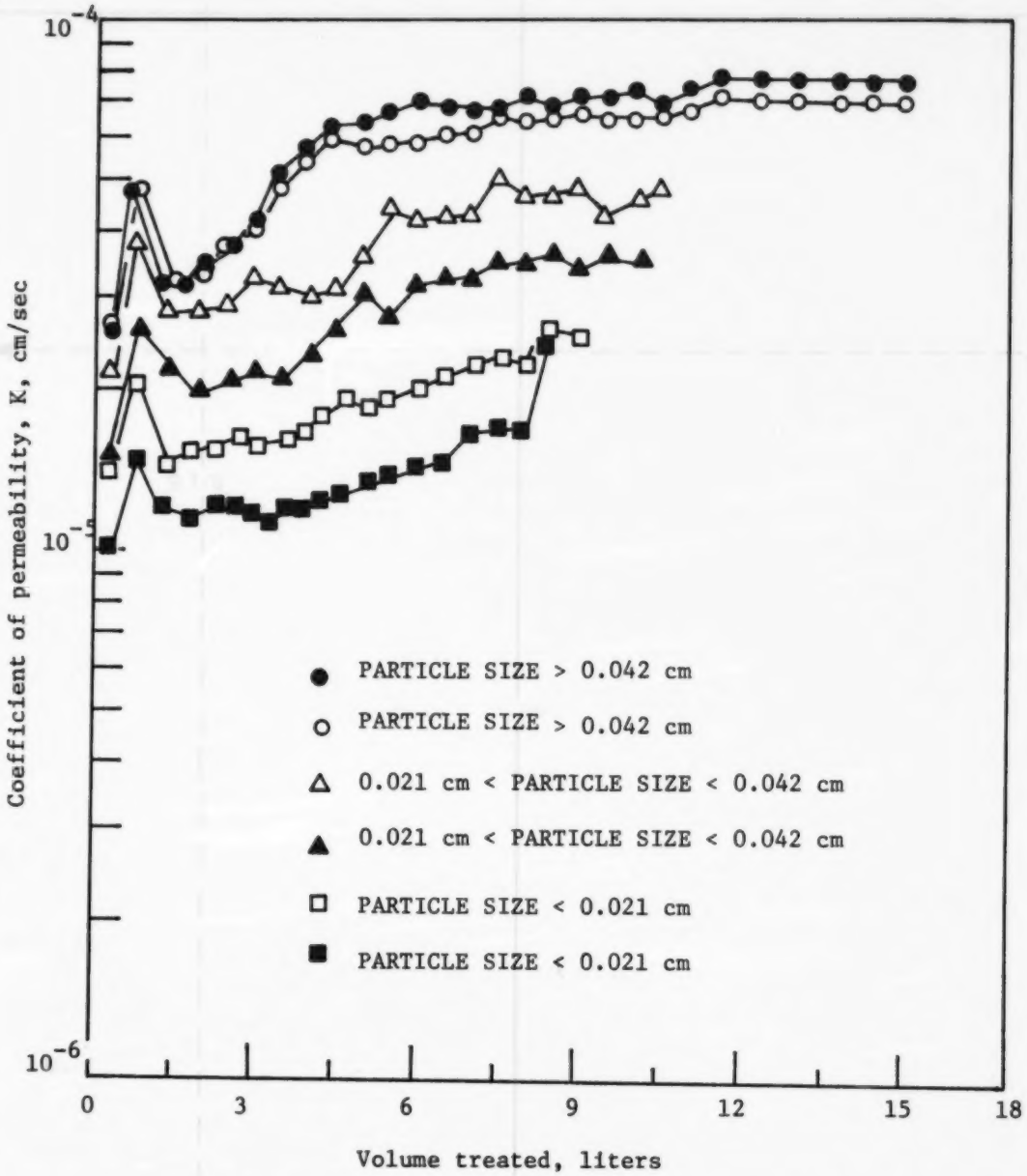

Figure 12. Sorbent particle size effect on permeability

Removal of Iron, Fluoride, Cadmium, Lead and Chromium

The analysis of one of feldspar wastewater samples (Sample No. 3) revealed that the concentrations of iron (0.3 mg/ℓ), fluoride (5.8 mg/ℓ), lead (0.12 mg/ℓ), chromium (0.05 mg/ℓ) and cadmium (0.015 mg/ℓ) were at levels that should be reduced (Table 1). Thus, not only was the removal of iron and fluoride, but also the removal of cadmium, lead and chromium examined under upflow expanded bed conditions at pH 6.3 using the above mixture of illite-basic fly ash and lime.

The iron in the feldspar influent was reduced from 0.3 mg/ℓ to 0.12 mg/ℓ with no suggestions of breakthrough even after 140 liters of wastewater were added to the lysimeters (Figure 14). This is comparable to concentration levels achieved in the lysimeter effluent under gravitational flow. Yet, the flows obtained with the expanded bed operation is some two orders of magnitude greater. However, there are some leaching of Fe, Pb, Cd, and Cr, from the illite encountered in the initial 10 liters of effluent collected from the lysimeter. This is indicated by the fact that the iron concentration in the effluent is higher than that in the influent (Figure 14). This should pose no problems in practice since our earlier studies (4) reveal that this initial leaching can be regulated by the addition of adequate amounts of either basic fly ash or natural zeolite to control this initial leaching from the illite.

The combination of illite-basic fly ash and lime was found to reduce the fluoride in feldspar influent from 5.8 mg/ℓ to below 1 mg/ℓ (Figure 15). The fluoride concentration in the effluent is comparable to that achieved under gravitational flow conditions (Figure 8). However, it should be noted that after approximately 40 liters of wastewater has been passed through the lysimeters, the fluoride concentrations in the effluent begins to increase until breakthrough is achieved after 140 liters of wastewater has been passed through the lysimeter. This results when the contact time between the sorbent and wastewater is not adequate. Whenever this occurs, a gradual rather than a rapid increase in the influent fluoride concentration to breakthrough is observed. The contact time in these lysimeters operated at flows of 22.4×10^{-3} ℓ/min was determined to be 1.6 hours which is significantly less than the 6 hours required for maximum removal of the fluoride.

The combination of illite-basic fly ash and lime was found to reduce the lead concentration in the lysimeter influent from 0.12 mg/ℓ down to approximately 0.013 mg/ℓ (Figure 16). The chromium concentration was reduced from 0.05 mg/ℓ down to approximately 0.015 mg/ℓ (Figure 17), and the cadmium was reduced from 0.015 mg/ℓ down to about 0.01 mg/ℓ (Figure 18). It should be noted that this is being achieved under slightly acidic conditions (pH = 6.3) and at flows that are some 2 orders of magnitude greater than that which can be achieved by gravity.

An examination of the results of the treatment of iron, fluoride, lead, chromium, and cadmium indicate that the fluoride treatment controls the process. An examination of Figures 14 through 18 reveals that only the fluoride ion exhibits breakthrough within 140 liters of influent added to

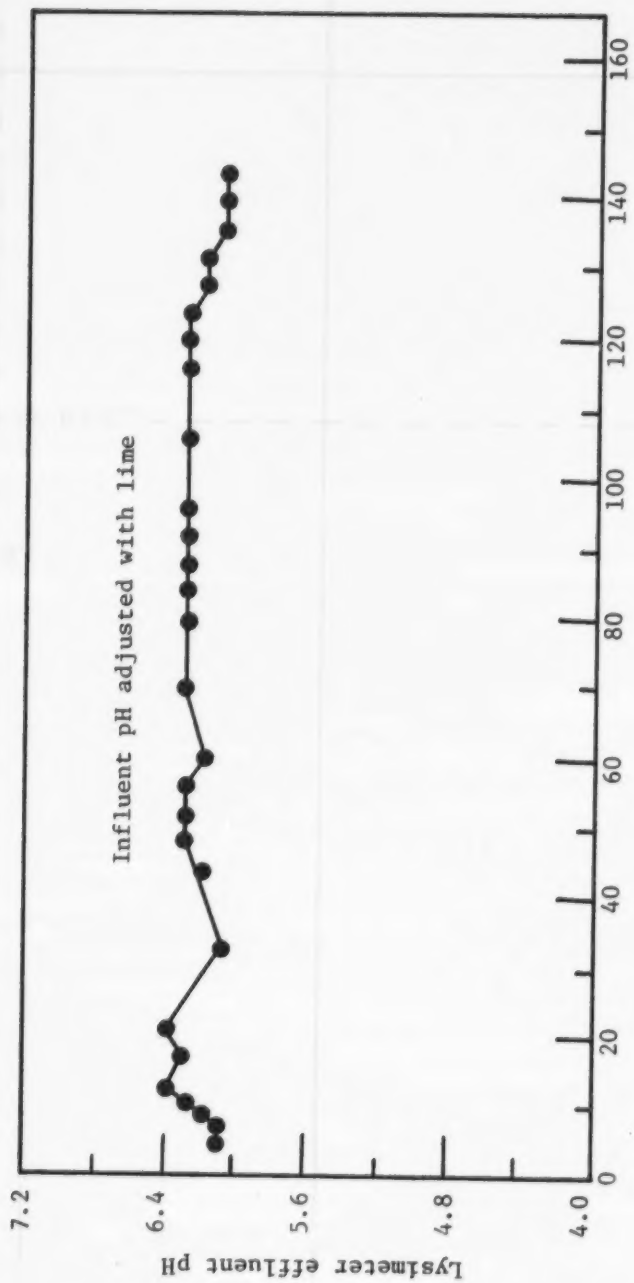

Figure 13. Effluent pH variations (expanded bed flow).

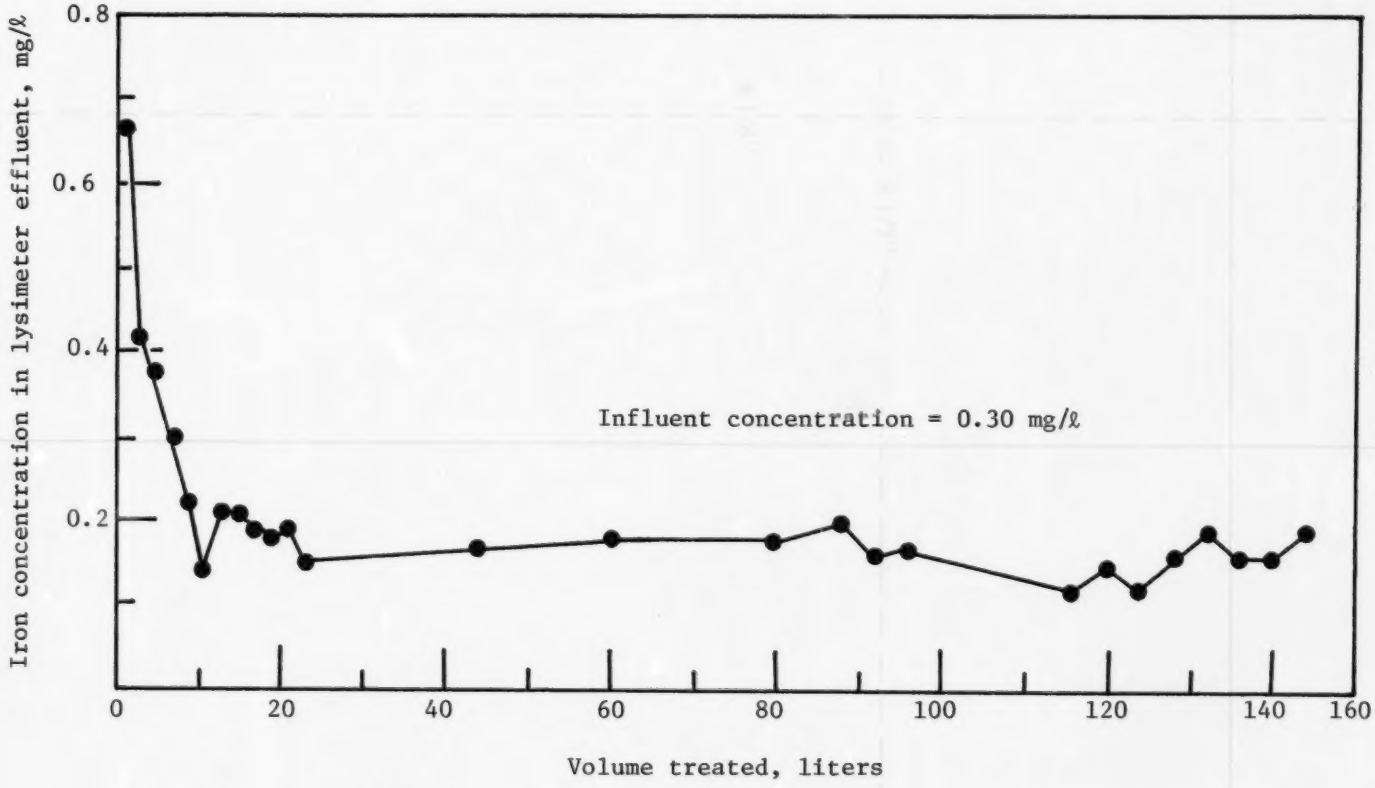

Figure 14. Iron treatment (expanded bed flow).

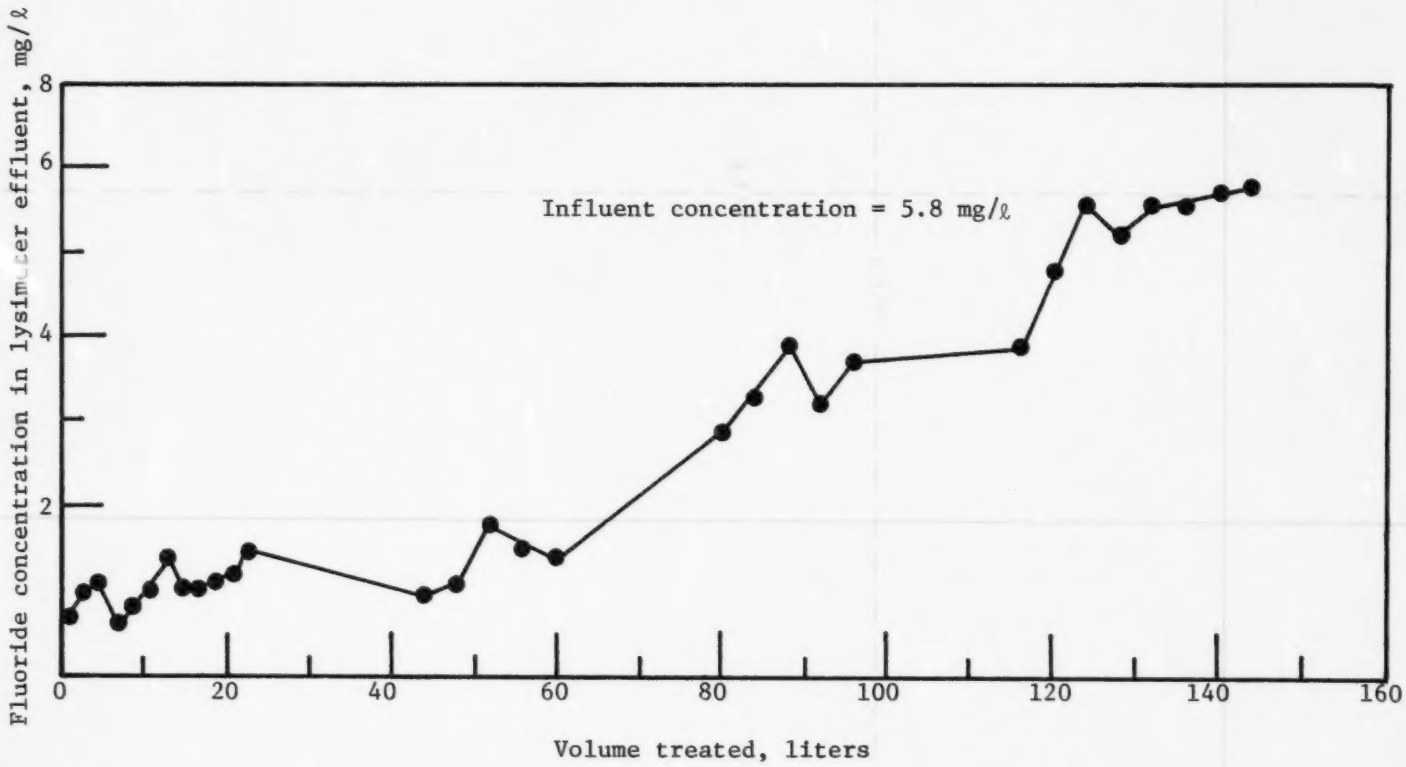

Figure 15. Fluoride treatment (expanded bed flow).

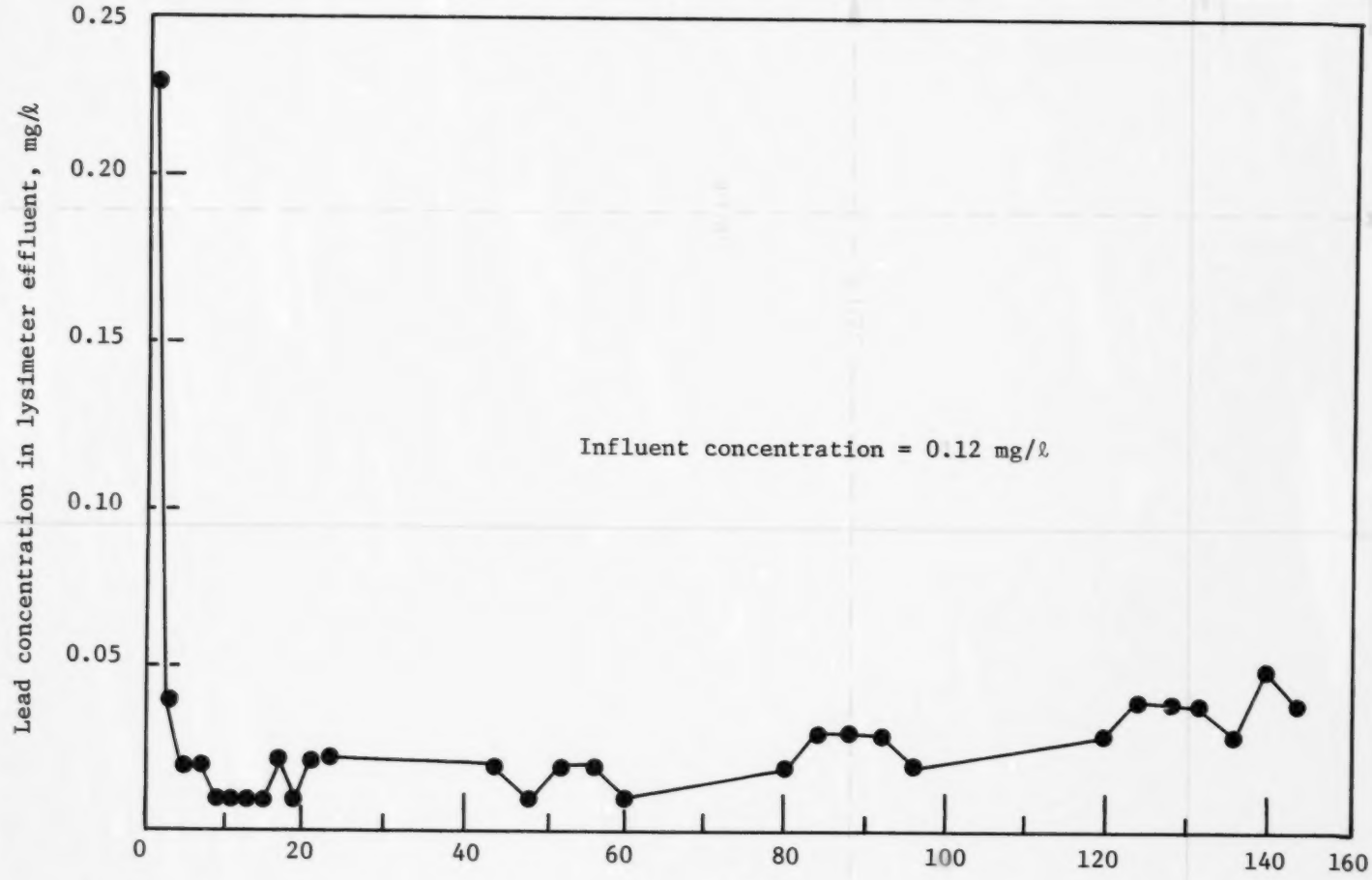

Figure 16. Lead treatment (expanded bed flow)

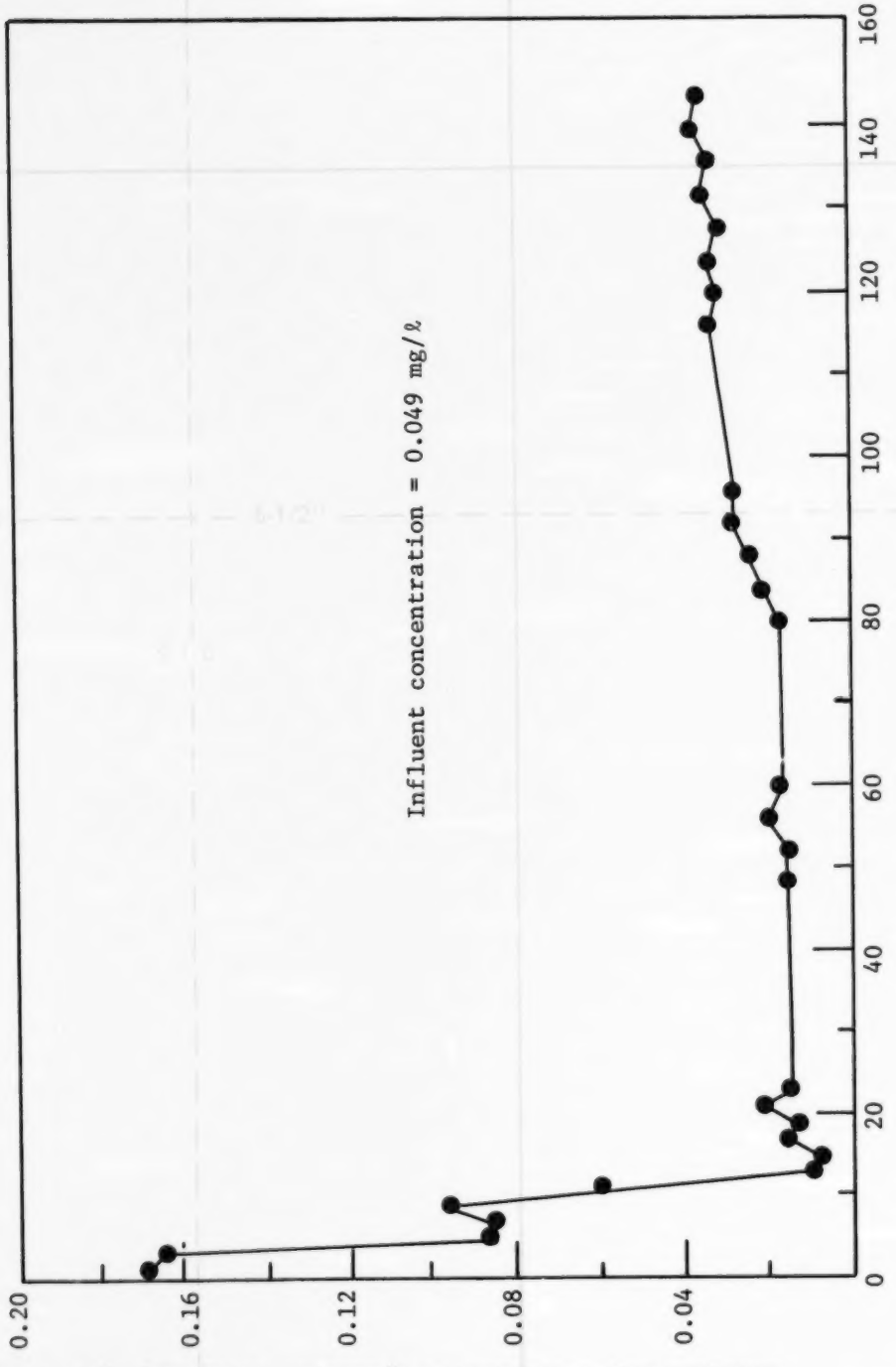

Figure 17. Chromium treatment (expanded bed flow)

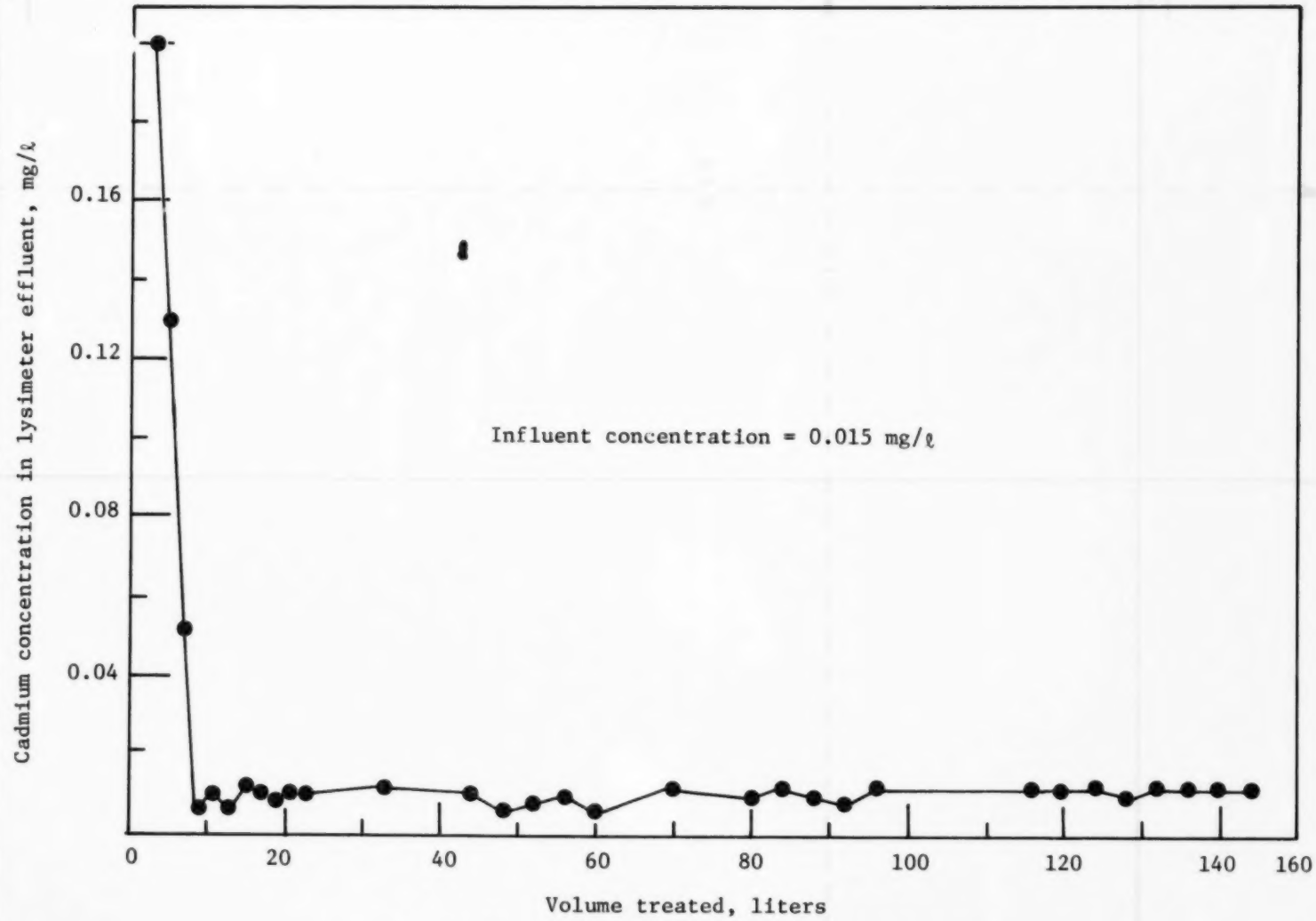

Figure 18. Cadmium treatment (expanded bed flow)

the lysimeters. Also, the characteristic increases in effluent concentration that is indicative of insufficient contact time between the sorbent and waste stream is observed only for the fluoride after 40 liters of waste stream has been passed through the lysimeter (Figure 15).

Sorbent Addition Versus Upflow Expanded Bed

It is apparent from the previous results that significant removals of iron, fluoride, lead, cadmium and chromium in the feldspar waste stream can be achieved. This treatment can be carried out by either adding the illite/fly ash/lime sorbent combination directly to the waste stream or by operating the sorbent bed in the upflow expanded bed mode. The addition of sorbent directly to the waste stream leads to better control of the concentration of pollutants in the treated effluent. The amounts of the sorbent combination that is added directly to the waste stream defines the pollutant concentration levels after treatment. However, with the use of sorbent beds maximum removals of the pollutants such as iron and fluoride occur. For example, the addition of 10 grams of sorbent directly to 1 liter of feldspar wastewater will reduce the fluoride from 5.8 mg/ℓ to a desired fluoride effluent concentration of 1.5 mg/ℓ, whereas the same amount of sorbent in a bed will reduce the effluent combination to below 1.0 mg/ℓ but treat only 0.9 liter of wastewater.

Settling Characteristics of Sorbent

The sorbents added to the waste can be removed in sedimentation basins provided that adequate settling rates are encountered. Settling tests carried out on the illite/basic fly ash/lime sorbent combination by measuring the interface between the suspension and clear liquid versus time results in a straight line (Figure 19). These results translate into a loading ratio of 1.78×10^4 ℓ/m^2/day (432 gal/ft^2/day) which is comparable to those generally encountered in the settling basins used in conventional municipal waste treatment systems.

Cost Comparison of Fluoride Removals Using Illite and Activated Alumina

The effectiveness of illite in reducing the fluoride ion concentration in the feldspar waste streams is compared to that achieved with activated alumina.

Maximum fluoride removal using activated alumina is strongly dependent upon pH as is the case for illite. In reducing the fluoride concentration from 25 mg/ℓ to 5 mg/ℓ, both activated alumina and illite exhibit maximum removal capacities at approximately pH = 6.3. However, at this pH, the removal capacity for activated alumina is 5 mg/gm as compared to 1 mg/gm for the illite (Figure 20).

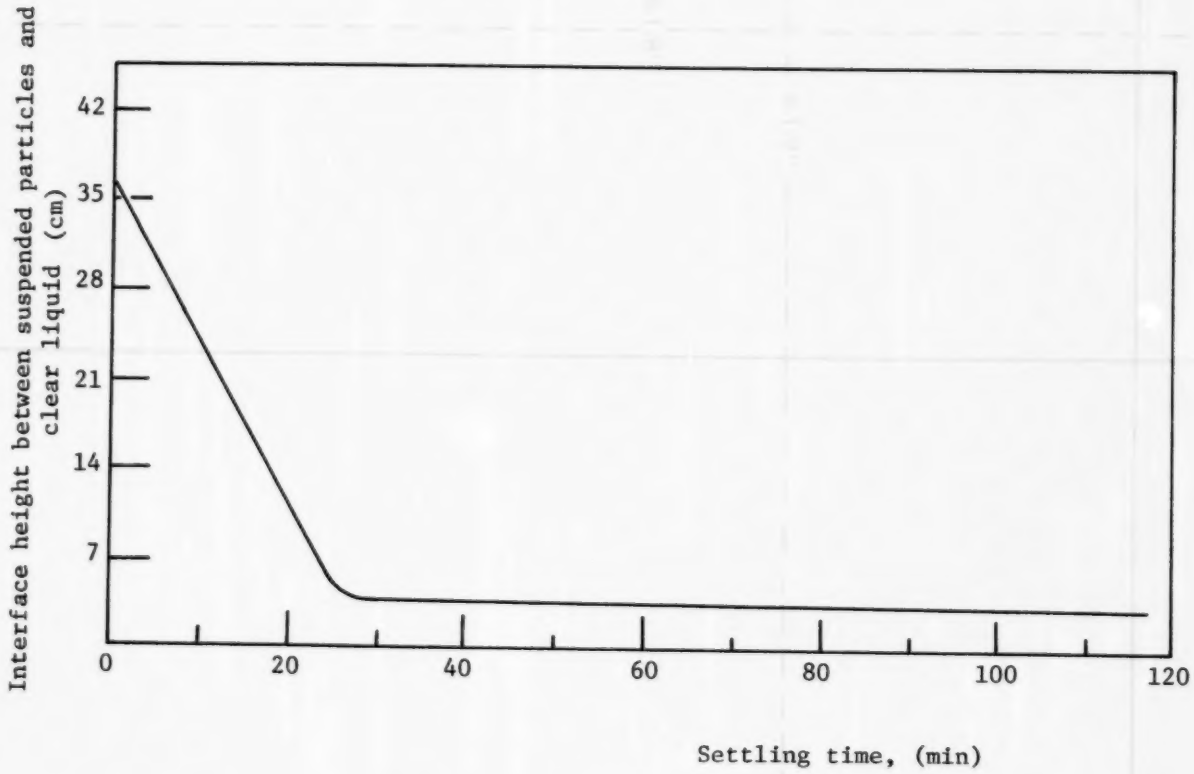

Figure 19. Settling characteristics of Sorbent

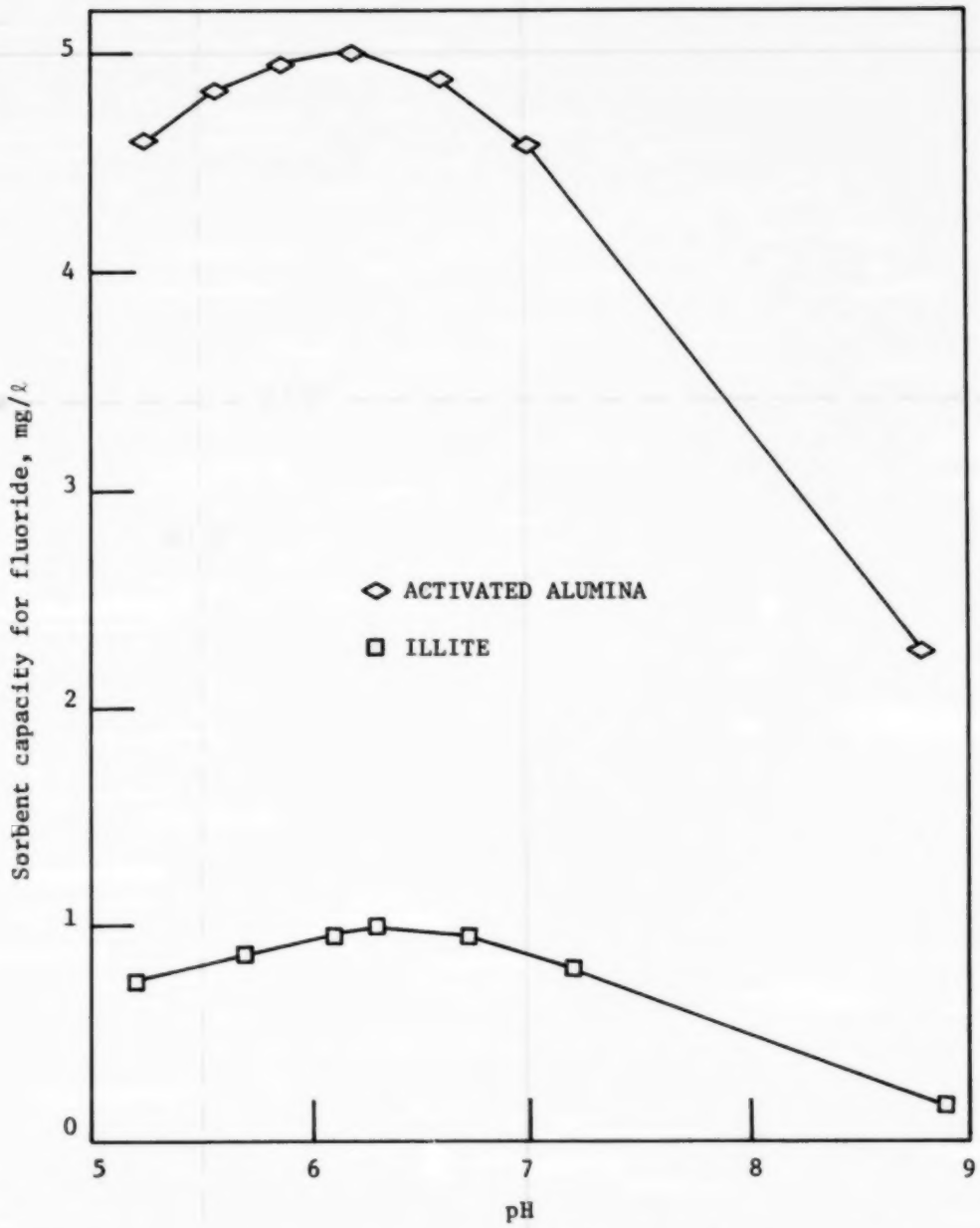

Figure 20. Activated alumina and illite sorbent capacity vs. pH (batch conditions)

In terms of material cost without regeneration of the sorbent, the use of illite is far less expensive than activated alumina for treatment of fluoride in the feldspar waste stream. The cost for illite is about $0.005 per lb., whereas the cost for activated alumina is about $0.30 per lb.. Thus, the material costs associated with the use of illite to obtain a fluoride effluent concentration of 5 mg/ℓ would be some 12 times less than that associated with the use of activated alumina, even though the activated alumina is five times more effective for removing the fluoride.

The use of activated alumina for the treatment of fluoride generally requires regeneration because of the high cost of alumina. The regeneration involves treating the spent activated alumina with sodium hydroxide followed by sulfuric acid to reduce the pH to 6.4 for maximum removal of fluoride. A calcium fluoride sludge is generated as a result of the treating of NaOH with calcium ion to precipitate the fluoride as CaF_2. Sulfuric acid is generally available at a feldspar mining and processing facility, but sodium hydroxide is not. Thus, the use of activated alumina requires additional facilities for storage of sodium hydroxide.

In comparison, the illite/basic fly ash/lime sorbent combination can also be regenerated but under acidic condition using sulfuric acid. NaOH is not required for regeneration. Five milliliters of 1 percent sulfuric acid solution per gram of illite (Figure 21) followed by lime treatment to bring the pH up to 6.3 for maximum removal of fluoride is required for regeneration of the sorbent. The initial regeneration of the sorbent results in approximately a 20 percent loss in its sorbent capacity for fluoride. Subsequent regeneration results in no measurable loss in the sorbent capacity (Table 2).

TABLE 2. SORBENT REGENERATION

Condition of sorbent	Sorbent capacity for fluoride (mg/g)
Original sorbent combination	1.00
1st regeneration of sorbent combination	0.81
2nd regeneration of sorbent combination	0.80
3rd regeneration of sorbent combination	0.80

Estimated Material Cost for Treating Feldspar Waste Streams

The fluoride concentrations in the feldspar waste stream generally averages about 6 mg/ℓ according to plant personnel at the site where the wastewater samples used in this investigation were collected. Material cost associated with the addition of the illite/basic fly ash/lime combination to the waste stream without regeneration to reduce the fluoride concentrations

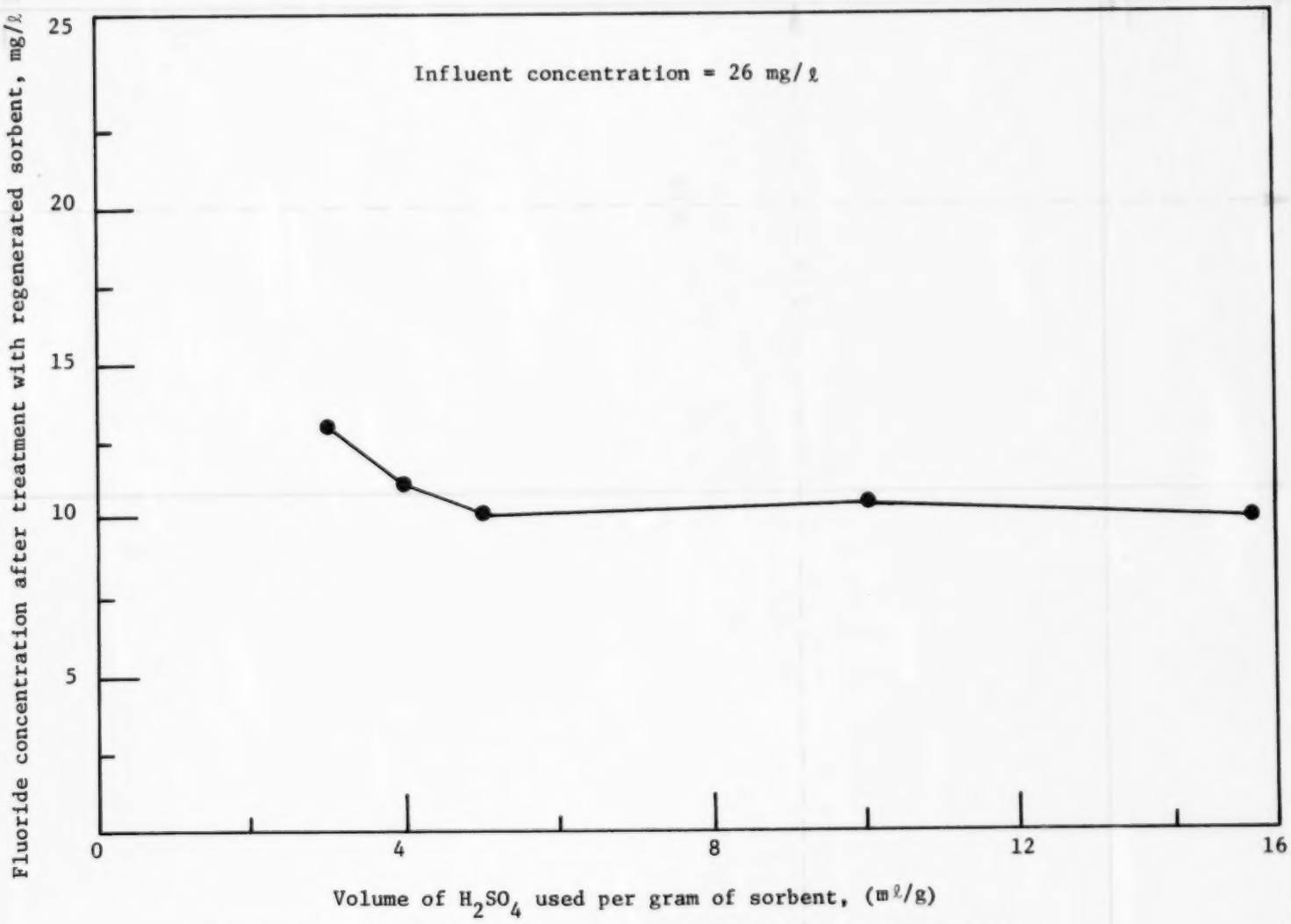

Figure 21. Fluoride treatment versus sulfuric acid regeneration

to 1.5 mg/ℓ is 45 cents per 3.8 x 10^3 liters (1000 gallons) or 78 cents per ton of feldspar produced (see Appendix). The spent sorbents can be discarded because the sorbed pollutants in the spent sorbents are held and released to the environment when in contact with water at levels that pose no threat to ground and surface waters. For example, repeated washing of a 10 gram and 20 gram of spent sorbent sample with 250 ml of water results in soluble fluoride concentrations in the initial washing that does not exceed 1.1 mg/ℓ (Table 3). Continued washing of the spent sorbent results in a decrease in the fluoride concentration in the rinse to below 1.0 mg/ℓ which is generally considered acceptable for potable water supplies.

TABLE 3. FLUORIDE CONCENTRATIONS IN SPENT SORBENT RINSE

	20 grams of spent sorbent		
Rinse No.	1 - 13	14 - 16	17 - 18
Conc. of fluoride in rinse, mg/ℓ	1.1	1.0	0.9

	10 grams of spent sorbent				
Rinse No.	1 - 3	4 - 7	8 - 10	11 - 14	15 - 18
Conc. of fluoride in rinse, mg/ℓ	1.1	0.8	0.6	0.4	0.3

Regeneration of the spent sorbents using sulfuric acid results in a reduction in material cost to 13.3 cents per 3.8 x 10^3 liters or 23 cents per ton of feldspar produced (see Appendix). However, the regeneration process results in the generation of a metal hydroxide, CaF_2, $CaSO_4$ sludge that must be disposed of when the spent sulfuric acid containing the fluoride and heavy metals is neutralized.

In comparison, the material cost associated with the use of activated alumina with regeneration to reduce the fluoride concentration in potable water supplies is twice as much. In 1953, the chemical cost associated with the removal of fluoride in the concentration range encountered in the feldspar waste stream using activated alumina with regeneration was reported to be 5.2 cents per 3.8 x 10^3 liters. If it is assumed that the average inflation rate for 26 years is 6 percent, the present chemical cost for this treatment is estimated to be 25 cents per 3.8 x 10^3 liters. A sludge also results that must be disposed of when the spent activated alumina is regenerated. The use of activated alumina without regeneration to avoid the sludge disposal problems would cost $4.95 per 3.8 x 10^3 liters (See Appendix).

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APPENDIX

MATERIAL COST FOR TREATMENT

1. Estimated material cost to reduce fluoride concentration in feldspar waste stream from 6 mg/ℓ to 1.5 mg/ℓ without regeneration of sorbents.

Sorbent Cost Without Regeneration to Treat 1000 Gallons of Feldspar Wastewater

Illite:

Total fluoride to be removed per 1000 gallons of wastewater = 1000 gal x 3.8 ℓ/gal x (6 mg/ℓ - 1.5 mg/ℓ) = 17100 mg

Sorbent capacity of illite/basic fly ash/lime sorbent combination for fluoride removal = 0.45 mg/g

Amount of illite required to treat 1000 gallons of wastewater 17100/0.45 = 38000 g = 83.7 lb/454 g/lb

Cost of illite per 1000 gallons wastewater treated = 0.5 x 83.7 = 41.9 cents

Lime:

A ratio of 1 part lime to 75 parts illite is required to provide a sorbent pH of 6.3

Amount of lime required to treat 1000 gallons of wastewater = 83.7 lb of illite (1/75) = 1.12 lb

Price of lime = $57.50/2000 lb

Cost of lime per 1000 gallons of wastewater treated = (5750/2000) x 1.12 = 3.2 cents

Total material cost to treat 1000 gallons of wastewater = 41.9 + 3.2 = 45 cents

Sorbent cost without regeneration per ton of feldspar produced

Assume:

Flow = 1 mgd

Feldspar production = 180×10^3 tons per year

312 days of operation per year

Total flow/year = 312×10^6 gallons

Cost/ton = 312×10^6 gallons/180×10^3 tons x 45 cents/1000 gal = 78 cents

2. Estimated material costs to reduce fluoride concentration in feldspar waste stream from 6 mg/ℓ to 1.5 mg/ℓ with regeneration. Cost for disposal of sludge produced during regeneration not included. Estimated material cost to use and regenerate illite/basic fly ash/lime spent sorbent combination as a result of treating 1000 gallons of wastewater.

Sulfuric acid costs 5 m of 1% H_2SO_4 is required to regenerate 1 g of sorbent

Amount of H_2SO_4 required to regenerate spent sorbents from treatment of 1000 gallons of wastewater

Sorbent capacity reduced from 0.45 to 0.36 after initial regeneration (17100/0.36 x 5 x 0.01/454 = 5.23 lb/1000 gal of wastewater

Price of H_2SO_4 = $40/ton = 2 cents per lb

Cost of H_2SO_4 per 1000 gallons wastewater treated = 2 x 5.23 = 10.5 cents

Cost of Lime:

5 ml of 0.17% CaOH solution per gm of illite is required to raise the pH of the sorbent to 6.3

Amount of lime required per 1000 gallons of wastewater = (17100/0.36) x 5 x 0.0017/454 = 0.89 lbs

Price of lime = 2.9 cents per lb

Cost of lime per 1000 gallons water treated = 2.9 x 0.89 = 2.6 cents

Total material cost associated with regeneration of spent sorbent combination from treatment of 1000 gallons of wastewater = 10.5 + 2.6 = 13 cents

Estimated replacement costs for illite and lime in treating 1000 gallons of wastewater assuming 100% sorbent replacement per year with spent sorbents being regenerated once every 2 days.

Illite:

Total fluoride removed in 2×10^6 gallons = 2×10^6 gal x 3.8 ℓ/gal x (6 mg/ℓ - 1.5 mg/ℓ) = 3.42×10^7 mg

The sorbent capacity for fluoride removed is reduced from 0.45 to 0.36 after the initial regeneration

Amount of illite required to treat 2×10^6 gallons of wastewater $3.42 \times 10^7 / .36 \times 1/454 = 2.1 \times 10^5$ lbs of illite required to treat 2×10^6 gallons of wastewater

Price of illite = $10/ton = 0.5 cents per lb

Cost of illite to treat 2×10^5 lb = $1050 sorbent cost/year assuming 100% replacement due to losses in regeneration in one year

Illite replacement costs per 1000 gallons = $1050/yr/$312 \times 10^6$ gal/yr x 1000 gallons = 0.34 cents

Lime:

A ratio of 1 part lime to 75 parts illite is required to provide a sorbent pH of 6.3

Amount of lime required to treat 2×10^6 gallons of wastewater 2.1×10^5 lbs (1/75) = 2.8×10^2 lbs

Price of lime = 2.9 cents per lb

Cost of lime to treat 2×10^6 gallons of wastewater = $0.029 \times 2.8 \times 10^2$ = $8.10

Lime replacement cost/1000 gallons = $8.10/yr/$312 \times 10^6$ gal/yr x 1000 gallons = 2.6×10^{-3} cents

Amount of sorbent replacement cost 1000 gallons assuming 100% replacement in one year = 0.34 + .003 = 0.34 cents

Estimate material cost for treatment of 1000 gallons of wastewater with regeneration

Regeneration cost (sulfuric acid and lime) = 13.0 cents/1000 gal

Sorbent replacement cost = 0.3 cents/1000 gallons

Total 13.3 cents per 1000 gallons

Estimated material costs with regeneration per ton of feldspar to treat 1000 gallons of wastewater

Assume flow = 1 mgd

Feldspar production = 180×10^3 tons/year

312 days of operation per year

Cost/ton = 312×10^6 gal/year/180×10^3 tons/yr x 13.3 cents/1000 gallons = 23 cents/ton of feldspar produced

Estimated material cost for use of activated alumina treatment without regeneration. To reduce the concentration in the feldspar waste stream fluoride from 6 mg/ℓ to 1.5 mg/ℓ in 1000 gallons.

Sorbent capacity of activated alumina was shown earlier to be five times that of sorbents = 0.45 x 5 = 2.3 mg/g

Total fluoride to be removed in 1000 gallons of wastewater (1000 gallons x 3.8 /gal x (6 mg/ℓ = 1.5 mg/ℓ) = 17100 mg

Amount of activated alumina required to remove 17100 mg of fluoride in 1000 gallons of wastewater 17100/2.3 x 1/454 = 16.5 lbs

Price of activated alumina = 30 cents per lb

Cost of activated alumina to treat 1000 gallons of wastewater without regeneration = 0.30 x 16.5 = $4.95